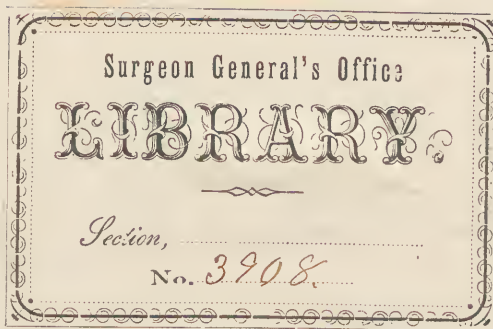


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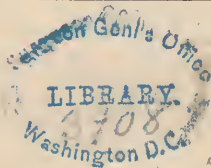
UNIVERSITY



CYCLOPÆDIA
OF
QUANTITATIVE CHEMICAL
ANALYSIS.

BY

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PREFACE TO PART I.

THE object of the author in compiling this book has been not only to provide the student and working chemist with a comprehensive dictionary of quantitative processes, but to call the attention of the chemical fraternity to the question of the possibility of presenting this branch of chemical art in a more serviceable and manageable form than has been customary hitherto. The experiment is certainly worth the trying whether a definite system of classifying substances in alphabetical order, and of referring each and every process to the fundamental fact or *principle* upon which it depends, will not greatly facilitate both the study and the practice of analysis.

The difficulty of perfecting the first edition of a work of this kind will be manifest to all. The author has consequently no apology to offer for the manifold shortcomings of his book. He wishes it to be understood distinctly that he has copied freely from the Handbooks of Rose, Fresenius, Berzelius, and Pfaff; from the Handwörterbuch der Chemie, and from the Dictionary of Watts. It is to be remarked, in that connection, that the similarity of wording in the descriptions of analytical processes in these various treatises is often so close that it would frequently be very difficult to determine precisely where credit should be accorded, or to judge how much credit should be given to each author. It is evident that in a subject which depends so nearly upon the precise statement of details, no compiler would be likely to depart far from the original description, as set forth by the inventor of a process. A good illustration of this inevitable tendency to repetition may be seen in the similarity of Pfaff's, Rose's and Fresenius's descriptions of Berzelius & Hisinger's process depending upon the insolubility of succinate of iron. References are given in all cases where matter has been taken from the journals and other original sources.

The manuscript of Part I. was completed, as now printed, in June, 1869. Nothing has been added to it, whether as regards matter or arrangement, from either of the treatises which have been published since that date, excepting the description, under Carbonate of Calcium, of Prof. Lawrence Smith's process for estimating alkalis,—copied from Prof. Johnson's edition of Fresenius's Quantitative Analysis, New York, 1870.

It is noteworthy that the tendency of all the works recently published on quantitative analysis is towards condensation and abbreviation, while the aim of the present book is to show that perspicuity can be best gained by amplification, if need be, and *methodical arrangement*. The author believes that the interests of chemists and of chemical students alike demand two kinds of books upon quantitative analysis. The one kind looking to completeness in all directions, while the other is given over either to specific instruction, or to the discussion of special applications of analysis in some one of the various departments of Chemistry.

It is not only important that the analyst should have a dictionary of all known methods, from which to choose the one which seems best to fulfil the conditions and requirements of any new problem which may come before him, but there will always

be needed books or tables devoted to schemes for illustrating the various kinds of analyses which are likely to occur in practice. Such, for example, as the works of Wolff and Caldwell, in the department of agricultural chemistry; or, in its day, the *Handbuch* of Pfaff, in the branch of mineral analysis. But if we were once in possession of a General Encyclopædia, covering the entire field of analysis, it would be easy to draw up long lists of these special schemes in very few words. For example:—

A residual product from some of the chemical works at Stassfurt, in Germany, sent into commerce to be sold as a fertilizer, contains the sulphates of potassium, magnesium and calcium; the chloride of potassium, sodium and magnesium; and a quantity of oxide of iron, magnesias and sand, insoluble in water. But the commercial value of any given sample of the substance depends upon the proportion of potassium which is contained in it.

Several methods have been employed for estimating the potassium,—after the matters insoluble in water have been got rid of by filtration. They might be briefly described as follows:—

A. Remove the SO_2 with BaCl_2 , as Sulphate of Barium; the Mg with BaO , H_2O , as Hydrate of Magnesium; the Ca and excess of Ba with $(\text{NH}_4)_2\text{O}$, CO_2 , as Carbonate of Barium, and estimate the K as Chloride and Chloroplatinate of Potassium.

B. Remove SO_3 by means of BaCl_2 , as Sulphate of Barium, decompose the Chloride of Magnesium with oxalic acid, and separate Mg as Oxide of Magnesium. Determine K as Chloroplatinate of Potassium.

C. Remove the SO_3 with BaCl_2 , as Sulphate of Barium; the Ba, Ca and Mg with Na_2O , CO_2 , as Carbonate of Barium, etc. Acidulate the filtrate with HCl and estimate K as Chloride and Chloroplatinate of Potassium.

D. Remove the SO_3 with BaCl_2 , as Sulphate of Barium, and estimate K in the filtrate as Chloroplatinate of Potassium (Stohmann's process).

The author of any such tables would of course give reasons why and when either of the processes would be preferred to the others.

In the appendix to the present work, a few examples for students' practice will be given in this sense.

N. B. All temperatures are given in degrees of the Centigrade thermometer,—excepting when otherwise expressly stated.

In the references to authorities, the larger figures indicate the volume, and the smaller figures the page, of the journal or work alluded to; single figures in parentheses () denote the number of the series of the journal.

The names of authors who have labored in concert are connected by the character &,—not by *and*.

To avoid the repeated printing of unnecessary words, cross references are indicated by printing in capitals the initial letters of the names of the substances referred to. Thus, on page 5, column 1, line 25, the capital initials in the words Oxide of Aluminum indicate that the article OXIDE OF ALUMINUM must be consulted, and that further information will be found under that head.

The names of rare elements have been omitted from this edition simply from lack of time to deal with them.

In order that the size and cost of the book might be kept within reasonable bounds, it has been thought best to exclude from it all figures of apparatus. The descriptions of unusual forms of apparatus have, however, been given in minute detail, and, in case of having to use any of this apparatus, the reader will do well to draw rough figures of it for himself with pen or pencil,—following the printed description, step by step. It is believed that if the descriptions be dealt with in this way, no great difficulty will be found in comprehending them, or in choosing that one among several processes which is best suited to the wants of the operator.

All ordinary implements and apparatus will be best understood from the descriptions given in works devoted specially to chemical manipulation.

Boston, July, 1870.

A CYCLOPÆDIA

OF

QUANTITATIVE CHEMICAL ANALYSIS.

Acetic Acid.

Principle I. Power of neutralizing alkaline solutions.

Applications. Estimation of free acetic acid in vinegar, pyroligneous acid and other aqueous solutions. (Method A). Determination of acetic acid in certain acetates from which caustic soda precipitates insoluble hydrates or oxides. (Method B).

Method A. A weighed or measured quantity (10 grms. of vinegar will be enough in most cases) of the solution to be examined is reddened slightly with litmus, and then treated with test-alkali until the whole of the acid is neutralized and the color of the litmus changed to blue. (See Acidimetry).

A solution of caustic soda is usually employed as the test-alkali, though solutions of carbonate of sodium were formerly much used. Greville Williams (*Pharm. Journ. Trans.*, 1854, 13. 594), has urged that a standard solution of lime in sugar water is to be preferred to soda, and Otto (in his *Lehrbuch der Essigfabrikation*, 1857, p. 77) has shown that dilute ammonia water may sometimes be employed with advantage. Other test-liquors are employed in particular cases, as will be described below.

The test-alkali is added to the acid under examination until the color of the litmus appears distinctly blue, or until a drop of the alkaline liquor is no longer seen to form a blue spot when it falls into the colored liquid.

It has been objected to the use of soda or of potash in estimating acetic acid, that the process must be inaccurate, since the normal acetates of the alkali metals themselves exhibit a slight alkaline reaction with litmus, or, at all events, change the color of litmus to violet. But as Otto (*Annal. Chem. und Pharm.*, 1857, 102. 71) has shown, the error from this source

is of but little significance. It was found not to exceed one-tenth of one per cent in determinations made with solutions containing ten per cent of the monohydrated acid, and is usually even smaller than this, since a slight excess of test-alkali is almost always added to the solution under examination. This source of inaccuracy may practically be eliminated by using a standard soda solution, the value of which has been determined beforehand by means of pure acetic acid. To prepare such a solution, measure off a determined quantity of standard sulphuric acid, mix it with a moderate excess of acetate of sodium, and determine how much of the standard soda solution is required to neutralize the acid mixture. By operating with a soda solution, whose power of changing red litmus to blue in presence of acetate of sodium has been thus determined empirically, the danger of error from the alkaline reaction of the acetate may be in great measure avoided.

According to Merz (*Journ. prakt. Chem.*, 101. 301), it is well to use a solution of turmeric instead of litmus as the indicator; for acetate of sodium has no action upon the color of turmeric. Enough of the turmeric solution is mixed with the acid to be tested to color it bright yellow; the liquid is heated nearly to boiling, and the soda solution stirred in rapidly until the moment when the color of the yellow liquid changes to brown.

According to Greville Williams, the best way is to dispense with soda altogether, and to employ in its place a solution of lime in sugar water (see Acidimetry); for acetate of calcium has not nearly so much power to disguise the action of acids upon litmus as the acetates of sodium and potassium have, to say nothing of the advantage which the lime solu-

tion necessarily possesses, in being at all times free from carbonic acid. For ordinary rapid work in testing vinegars, Williams finds that the process may be fully relied on to one-fourth of one per cent.

In testing crude pyroligneous acid, or highly colored vinegar, the color of the litmus added to the liquid is so much obscured towards the close of the operation by the impurities with which the acid is charged, that the exact point of neutralization cannot be determined by mere inspection of the liquid. It is necessary, as the point of saturation approaches, to test the liquid with litmus paper. To this end, after each fresh addition of the alkali, the point of the glass rod used for stirring is drawn across a narrow sheet of litmus paper, and from the color of the mark thus formed, the progress of the neutralization is inferred. When the paper ceases to be reddened by the liquid, the operation is finished. For some eyes turmeric paper may be advantageously substituted for the litmus paper. A brown spot or ring will form upon the yellow paper as soon as the acid has all been neutralized and the slightest excess of free alkali is present in the liquid.

In the case of vinegars so highly colored that the point of neutralization cannot be satisfactorily determined even with litmus paper, the proportion of acetic acid may be found, according to Carl Mohr, as follows:—Boil a measured sample of the vinegar with a weighed excess of carbonate of barium until no more carbonic acid is given off. Separate the dark colored, soluble acetate of barium by filtration; throw the moist filter, with its contents of carbonate of barium into a beaker, and pour upon it a measured volume of standard nitric acid, more than sufficient to dissolve the whole of the carbonate. Finally determine the free nitric acid with a standard solution of soda, and calculate the proportion of acetic acid from the quantity of carbonate of barium which the nitric acid dissolved. The process is evidently liable to error, inasmuch as acetic acid is readily volatile at the temperature of boiling.

F. Mohr (*Titrimethode*, 1855, p. 362) claims to have obtained good results in estimating acetic acid by means of the standard solution of ammonio-sulphate of copper, proposed by Kieffer (see Acidimetry), as a substitute for test-alkali. In using this solution, however, the acetic acid must be so highly diluted that a precipitate shall form immediately, from the very first, at the point where the test solution comes in contact with the acid liquor. The close of the operation will be indicated by the fact that the precipitate ceases to redissolve when stirred. Unless the acid be very dilute, considerable quantities of the sub-salt of copper will remain dissolved in the acetate of copper which forms. It may even happen that the solution of acetic acid can be made strongly

alkaline, although no precipitate has been seen to form in it. Mohr directs that the beaker which contains the diluted vinegar be placed on a black ground, and that the operator, while stirring the liquid, should look into it from above. — Another method, somewhat related to that of Kieffer, is to use a copper salt as the indicator instead of litmus. A few drops of a solution of pure sulphate of copper are added to the vinegar, and a standard solution of soda is poured into the mixture until the moment when a faint persistent cloudiness, due to precipitated hydrate of copper, appears in the liquid. The point of saturation may be readily hit in this way in vinegars which are transparent and free from suspended matters, even though they be somewhat colored.

Instead of the processes above referred to, which are of comparatively recent invention, vinegar makers have long been accustomed to determine the strength of their products by means of carbonate of sodium or carbonate of potassium. According to Otto, the method of procedure is as follows:—Select a suitable number of clear, transparent, non-effloresced crystals of hydrated carbonate of sodium, rub them to coarse powder in a mortar, and preserve the powder in a tightly stoppered bottle. Weigh out in a capacious flask or beaker fifty grms. (custom prescribes 2 Troy ounces = 960 grains) of the vinegar to be tested, and add to it a couple of drops of a solution of litmus. Set the flask in an inclined position upon a wire gauze support and heat it moderately with a lamp. Put 30 or 40 grms. (or about a Troy ounce) of the powdered carbonate of sodium in a weighing tube and counterpoise the tube with its contents upon a balance. By means of a small spoon or spatula, take portions of the carbonate of sodium from the weighing tube and carefully throw them into the warm vinegar in the flask until the red color of the vinegar is changed to blue. When the point of neutralization has been reached, replace the weighing tube with the unused portion of its contents upon the balance, and by adding weights to make good the loss, determine how much of the carbonate has been required to effect the neutralization. The quantity of acetic acid in the solution tested is readily obtained by the following proportion:—

$$\begin{array}{l} \text{Molec. weight} \\ \text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O} \end{array} : \begin{array}{l} \text{Molec.} \\ \text{weight} \\ \text{of} \\ \text{Acetic} \\ \text{Acid} \end{array} = \begin{array}{l} \text{Weight of} \\ \text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O} : x \\ \text{used} \end{array} \left(= \begin{array}{l} \text{Wt. of} \\ \text{Acetic} \\ \text{Acid} \\ \text{in the} \\ \text{Sample.} \end{array} \right)$$

The molecular weight of acetic acid in the second term of the proportion may be derived either from the formula $\text{C}_2\text{H}_4\text{O}$ (anhydrous acetic acid), or $\text{C}_2\text{H}_4\text{O}_2$ (monohydrated acetic acid), according as the strength of the sample is to be expressed in terms of anhydrous or of hydrated acid. In practice, the strength of acetic acid is stated sometimes in one way, and sometimes in the other. In case 2 ounces = 960 grains of vinegar, are taken, every 27

grains of crystallized carbonate of sodium required to effect neutralization will represent one per cent of anhydrous acetic acid, or every 22.8 grains one per cent of the monohydrated acid.

To avoid loss of material during the tumultuous ebullition caused by the evolution of carbonic acid, care should be taken that the flask or beaker in which the vinegar is heated is never more than about a quarter full of the liquid. The carbonate of sodium should be taken up by small fractions, and no new portion of it should be added to the liquid until the last portion has ceased to give off gas. Just before each fresh addition of the carbonate the liquid should be shaken in such manner that any drops of it which may have been thrown against the upper side of the inclined vessel shall be washed down into the main body of liquor. The spoon used for transferring the carbonate of sodium should be kept as dry as possible. In case the steam from the flask wet it, it should be rinsed at the mouth of the flask with a wash bottle and afterwards dried.

As long as the color of the solution remains bright red, the carbonate of sodium may be added with freedom and rapidity; but when the point of neutralization is near at hand, only very small portions of the carbonate should be added. In any event the color of the liquid serves merely as a rough indication of the progress of the experiment. Litmus paper must be used as a test of thorough saturation. As soon as the color of the solution becomes obscure, small drops of the liquid must be placed upon litmus paper after each addition of the carbonate, until the paper ceases to be reddened, or is actually turned blue. It is not best to color the vinegar intensely red at the start. Two or three drops of litmus will color it sufficiently. When the vinegar is strongly reddened at first, it is apt to acquire a violet tint towards the close of the operation which tends to obscure the reaction of the solution upon paper. In case the vinegar is strongly heated, it is best not to add any litmus to it until the comparatively sluggish evolution of carbonic acid indicates that the point of neutralization is almost reached. The crystals of carbonate of sodium chosen for this use should be free from any spots of efflorescence. Instead of crystals of sal-soda, some vinegar makers prefer to use the anhydrous, recently ignited carbonate. In any event, carbonate of sodium is to be preferred to carbonate of potassium, although the latter, at one time exclusively employed, is still sometimes used. The use of standard solutions of carbonate of sodium is not to be commended. They are inferior in all respects to solutions of the caustic alkalies. It has been already mentioned that Otto recommends the use of ammonia water four or five times diluted, chiefly because this liquid may be readily obtained of

any druggist. For a description of a graduated instrument specially devised for the use of vinegar makers, in which vinegar may be neutralized with standard ammonia water, see Otto's *Lehrbuch der Essigfabrikation*, p. 77 et seq.

An old method of testing vinegar was as follows:—Weigh a lump of pure, dry marble, place it in a measured quantity of vinegar, insufficient to dissolve the whole lump, and warm the liquid slightly, until all the acid is saturated with calcium. Wash the undissolved portion of marble with boiling water, dry it at the same temperature as before, and again weigh it. From the loss of weight calculate the amount of acid in the sample examined. Objections to this process are found in the difficulty of washing out the acetate of calcium from the porous stone as well as in the slow action of acetic acid upon marble, and the impossibility of bringing the marble to absolutely the same state of dryness before and after the action of the acid. (Gr. Williams, *Pharm. Journ. Trans.*, 1854, 13. 595).

Method B. To determine acetic acid in acetates from which caustic soda precipitates hydrates or oxides, such as ferric acetate or acetate of copper, mix a weighed quantity of the acetate with a measured quantity of a standard solution of caustic soda or carbonate of sodium, more than sufficient to decompose the whole of the acetate. Heat the mixture to boiling, collect the precipitate upon a filter, wash it with hot water, concentrate the filtrate to a convenient bulk and determine the excess of alkali with standard acid. The difference between the amount of soda thus found and the amount of soda taken, gives the quantity of soda which has been neutralized by the acetic acid in the substance analyzed. The amount of acetic acid is found by the proportion:—

$$\begin{array}{l} \text{Molec. wt. of NaHO} \cdot \text{Molec. wt. of C}_2\text{H}_3\text{O}_2 = \text{Wt. of Soda} \\ \text{neutralized} \end{array} : x = \left(\frac{\text{Wt. of acid}}{\text{in sample}} \right)$$

Care must be taken that none of the acid is lost by precipitation as a basic acetate in the first instance. Since a good deal of carbonic acid would be absorbed from the air during the evaporation of the filtrate in case caustic soda were employed, it is as well to use a standard solution of carbonate of sodium. (See Acidimetry).

To determine the unused excess of alkali, the solution may be heated to boiling, colored with litmus, and directly saturated with standard acid; or an excess of standard acid may be added at once, the solution boiled to expel carbonic acid, reddened with litmus, and then treated with a standard solution of caustic soda until a blue tint is imparted to it.

Unlike most of the other acids, the strength of a solution of acetic acid cannot be determined by taking the specific gravity of the solution. Not only are the differences in density corresponding to different proportions

of acid very small,—ranging only from 1.057, the specific gravity of glacial acetic acid, to 1.000, the specific gravity of water,—but the differences are not regular, or directly proportional to the amounts of acid in the solution. Thus the specific gravity of a solution containing only 37 per cent of anhydrous acetic acid is almost absolutely identical with that of a solution containing 85 per cent. Solutions of vinegar and of crude pyroligneous acid are often met with, moreover, charged with varying proportions of other soluble substances, so that this method of estimation would not admit of general application in any event.

The strength of pure vinegars made from diluted alcohol, whiskey, or other distilled spirit, may, however, be tested with the hydrometer indirectly, as follows:—Add dry slaked lime to a measured quantity of the vinegar, to alkaline reaction, or, better, until the color of the solution suddenly changes to yellow or brown, while a flocculent precipitate forms in the liquid. This change of color, due to the presence of impurities in the vinegar, indicates that an excess of lime has been added. Cool the solution of acetate of calcium to 15° and test it with a hydrometer. By reference to a table of specific gravities and percentage composition of solutions of acetate of calcium, the proportion of this salt and, therefore, the proportion of acetic acid, may readily be obtained. The process is well adapted for technical determinations. (Ordway, *Amer. Journ. Sci.*, 1861, **31**, 451). It was formerly employed in England by excise officers, but could hardly have afforded accurate results with vinegar made from malt, cider, etc., on account of the various soluble mucilaginous substances with which such vinegar is charged.

Principle II. Volatility.

Application. Estimation of the acid in crude acetate of calcium.

Method. Weigh out about 5 grms. of the acetate of calcium, place it in a small tubulated retort, together with 50 c.c. of water and 50 c.c. of ordinary phosphoric acid of about 1.2 specific gravity, free from nitric acid. Set the retort on a wire gauze support in such a position that its neck may slope slightly upwards. By means of tightly fitting corks and a delivery tube, connect the mouth of the retort with a small Liebig's condenser, and distil almost to dryness. Collect the distillate in a quarter-litre flask, taking care that none of it is lost. Allow the retort to become cold, pour into it 50 c.c. more water, again distil almost to dryness, and afterwards repeat the operation yet a third time. Add water to the distillate by small portions, agitating the mixture after each addition, until the flask is filled up to the quarter-litre mark. Then draw off portions of 50 c.c. or 100 c.c. with a pipette, and determine the acid contained in them by means of a normal solution of caustic soda, as described in A. In case the acetate of calcium

is contaminated with a chloride, the salt may be distilled with chlorhydric instead of phosphoric acid. The proportion of chlorhydric acid in the distillate would in that case be determined by titrating one portion of it with a solution of silver (see Chloride of Silver), after the total amount of acetic acid and chlorhydric acids had been determined in another portion with standard soda. The proportion of acetic acid would then be inferred from the difference. Sulphuric acid cannot readily be employed, since sulphurous acid is formed through its action upon organic matters attached to the acetate of calcium. (Fresenius, *Zeitsch. Analyt. Chem.*, 1866, **5**, 315).

Principle III. Feeble solvent action; or rather, power of dissolving certain substances without acting upon others.

Applications. Acetic acid is used to acidulate liquids in many cases where stronger acids are inadmissible. See, for example, Acetate of Aluminum, Acetate of Iron, Chromate of Barium, Phosphate of Iron, Phosphate of Uranium, etc., etc.

The commercial acid of 1.04 specific gravity, containing about 25 per cent of the anhydrous acid, is usually pure enough and strong enough for purposes of analysis. It should be tested with solutions of nitrate of silver, nitrate of barium, and of indigo; with sulphuretted hydrogen, and with ammonia water and sulphhydrate of ammonium before use, in cases where the presence of chlorine, sulphuric acid, nitric acid, sulphurous acid, or of either of the heavy metals would be prejudicial. If pure, the acid will neither leave any residue when evaporated on platinum foil, nor emit an empyreumatic odor on being heated after having been saturated with carbonate of sodium.

In order to purify an impure acid, mix it with some acetate of sodium, and slowly distil the liquid almost to dryness in a glass retort. In case sulphurous acid has been detected by the deposition of sulphur on testing with sulphuretted hydrogen, digest the acid for some time with binoxide of lead or precipitated binoxide of manganese, and decant the clear liquid before adding the acetate of sodium.

Acetate of Aluminum.

Principle. Insolubility in water of certain basic acetates of aluminum. These acetates separate when neutral or nearly neutral aqueous solutions of acetate of aluminum, which contain some other salts, are heated. (Compare Dictionary of Solubilities).

Applications. Determination of aluminum in most compounds of aluminum with inorganic or volatile organic acids, which are soluble in water or chlorhydric acid. Separation of Al from Li, K, Na; Ba, Ca, Sr, Mg, Mn, Ur, Fe (see Method B.), Co and Zn; less completely from Ni. The method is employed more particularly when both Al and Fe have to be separated together from the other metals.

Method A. Put the cold, moderately dilute,

somewhat acid solution in a flask or beaker, and add to it carbonate of sodium by small lumps, or ammonia water little by little, until the acid is so nearly saturated that on shaking the liquid the precipitate formed by the last addition of alkali barely dissolves. Add to the clear, cold liquid a few drops of acetic acid, and then pour in as much of a strong aqueous solution of normal acetate of sodium, or acetate of ammonium, as may be needed to convert by double decomposition all the bases present into normal acetates. Heat the mixture to boiling, and continue to boil for a short time. If the operation has been properly conducted, the precipitate will settle readily from the liquid in the form of transparent flocks, when the lamp is removed.

Pour the clear, hot liquor upon a filter, wash the precipitate two or three times by decantation with boiling water, to which some acetate of sodium, or acetate of ammonium, has been added; transfer the precipitate to the filter and finish the washing on the filter with boiling water. — The precipitate is dried, ignited and weighed as Oxide of Aluminum, with the precautions prescribed under that head. Or, in case peculiar accuracy is required, the moist precipitate is dissolved in chlorhydric acid and again thrown down with acetate of sodium, to remove the last traces of the stronger bases.

Method B. In separating iron from aluminum by this process, the two elements are thrown down together as basic acetates. The mixed precipitate is ignited with the precautions enjoined under Acetate of Iron, and weighed as alumina plus ferric oxide. The proportion of iron is then determined by titration. (See *prot Oxide of Iron*). The difference between the weight of ferric oxide thus obtained and that of the mixed precipitate, gives the weight of the alumina.

Precautions. According to Gibbs & Atkinson (*Amer. Journ. Sci.*, 1865, 39. 60), the metals in the original solution had better be in the form of chlorides. If the original solution contains any considerable excess of acid, this excess should be removed by evaporation, and the solution again diluted with water before adding the carbonate of sodium or the ammonia. The solution should be so dilute that a litre of it would contain no more than two grms. of Al_2O_3 , or of Al_2O_3 plus Fe_2O_3 , in case both iron and aluminum were present. In case the liquid become turbid through the addition of too much alkali, it should be made clear again by the least possible quantity of chlorhydric acid before proceeding to add the acetic acid and acetate of sodium. After boiling the mixture, it should be filtered hot, for if the supernatant liquid were left to cool in contact with the precipitate, some of the latter would dissolve. For the same reason, it is best to employ a plaited filter and to allow the filter to become empty after each addition of liquid before refilling it. The boiling must not be too

long continued, lest the hydrate of aluminum become slimy and stop the pores of the filter. Unless a considerable excess of acetate of sodium be employed, an appreciable quantity of aluminum will escape precipitation; the precipitate, in this case, has a peculiar granular appearance. In case the filtration is slow, some aluminum will pass into the filtrate, and may be separated therefrom on boiling. This subsidiary precipitate should be collected on a separate filter. — The precipitate usually retains insignificant traces of soda, but should not exhibit a strong alkaline reaction when moistened with water after ignition. In case the presence of sodium salts in the filtrate is undesirable, ammonia-water and acetate of ammonium must be employed instead of the carbonate and acetate of sodium. — Though the precipitate cannot be very conveniently filtered and washed, and though traces of aluminum always remain in the filtrate, the process affords satisfactory results when carefully executed. It is less esteemed, however, than the corresponding process for determining iron. (See Acetate of Iron). The analogous process based upon the insolubility of basic Formiate of Aluminum is preferable, inasmuch as the formiate may be washed more readily than the acetate.

Acetate of Barium.

Principle. Power of precipitating sulphates and chromates. Compare Acetic Acid (feeble solvent power of).

Applications. Acetate of barium is used as a reagent to precipitate sulphate of barium or chromate of barium in cases where the presence of chlorhydric or nitric acid would be inadmissible. To prepare the acetate, dissolve pure carbonate of barium in moderately dilute acetic acid, filter, evaporate and set the strong solution aside to crystallize; keep the dry crystals for use.

Acetate of Iron (Ferric Acetate).

Principle I. Insolubility in water of certain basic acetates of iron. These acetates separate when neutral, or nearly neutral, aqueous solutions of ferric acetate, which contain some other salts, are boiled. (Compare Dictionary of Solubilities).

Applications. Determination of iron in salts of iron, with most inorganic or volatile organic acids, which are soluble in water or chlorhydric acid. Separation of Fe from Li, K, Na; Ba, Ca, Sr; Mg, Ur, Al, Mn, Co and Zn; less completely from Ni. Separation of Fe_2O_3 from FeO. (Method B).

Method A. Similar in all essential particulars to that described under Acetate of Aluminum.

Precautions. According to Fresenius, the success of the operation depends on the iron solution being sufficiently dilute, and the free acid sufficiently neutralized, as well as upon the presence of a sufficient excess of acetate

of sodium. If these conditions are complied with, all the iron will be thrown down as soon as the liquor boils. It is not necessary in any event to boil the mixture longer than two or three minutes.

Unless it is intended to separate FeO from Fe_2O_3 (as in Method B), the iron must all be in the condition of a ferric salt before the liquid is neutralized. After the addition of the carbonate of sodium, or the ammonia-water, the liquid should assume a deep brownish-red color, but no permanent precipitate should be allowed to form in it before the alkaline acetate is added. The filtration should be rapid, as with the aluminum salt, and the supernatant liquor should not be allowed to cool in contact with the precipitate. If, after boiling, the mixture were left to itself for several hours, a small quantity of iron would go into solution.

Sometimes, though not often, portions of the precipitate pass mechanically through the pores of the filter, and have to be collected upon another filter after standing six or eight hours. The washed precipitate had better be dissolved in chlorhydric acid while still moist, and the iron reprecipitated with ammonia as a hydrate. If the precipitate is small, however, it may be ignited and weighed directly as Oxide of Iron, taking care to oxidize any ferrous-ferric oxide which may form, by a final ignition in oxygen gas, or with addition of nitric acid. The process is convenient, and affords accurate results, though the corresponding process with Formiate of Iron is said to be preferable, inasmuch as formiate of iron is more readily washed than the acetate.

Method B. To separate Fe_2O_3 from FeO , Reichardt (*Zeitsch. analyt. Chem.*, 1866, 5, 63, 64) mixes the hot chlorhydric acid solution of the two oxides with a tolerably large quantity of chloride of ammonium, dilutes the mixture largely with boiling water, neutralizes the hot solution with ammonia, and immediately re-dissolves the precipitate with a few drops of chlorhydric acid. The clear liquid is then heated to actual boiling, immediately removed from the fire and treated with an excess, but not too large an excess, of crystals of acetate of sodium. In a very short time after the crystals have been stirred into the liquor, all the iron in the ferric salt will separate as a flocculent precipitate, which may be filtered immediately and washed with boiling water. The province of the chloride of ammonium is to hinder the oxidation of the ferrous salt. It accomplishes this purpose so well that the filtrate from the precipitated ferric acetate might be left standing in the air for hours and still remain clear and colorless. To determine the proportion of ferrous oxide:—Heat the filtrate to boiling, add chlorhydric acid, drop by drop, until the liquid remains permanently clear; throw in small crystals of chlorate of potassium until a drop of the liquid no longer yields a blue color when tested with ferri-cyanide of

potassium, remove the boiling liquid from the lamp, and stir into it crystals of acetate of sodium as before, to precipitate the ferric oxide. If the oxidized solution contains no substance, besides ferric oxide, precipitable by ammonia in presence of ammonium salts, the iron may of course be thrown down as Hydrate of Iron in the usual way.

Manganous oxide, or a mixture of manganous and ferrous oxides, may be separated from ferric oxide in a similar way by mixing the original chlorhydric acid solution with chloride of sodium, and hydrate or carbonate of sodium, in place of the chloride of ammonium and ammonia water just described. The FeO and MnO are subsequently oxidized with chlorate of potassium to Fe_2O_3 and Mn_2O_3 , and the Fe_2O_3 thrown down by means of a new portion of acetate of sodium.

Reichardt recommends that the acetate of sodium be added in all cases in the form of crystals, as above described, after the boiling liquid has been removed from the lamp, even when iron is to be separated from the alkaline earths, and from phosphates of the alkaline earths. According to him, boiling as directed in Method A renders the precipitate more difficult of filtration, besides being objectionable on other accounts.

Principle II. Colorific Power.

Applications. Estimation of small quantities of iron, as in the analysis of rocks.

Method. A special instrument known as a colorimeter is required. (See Colorimetry). For a description of the process of analysis, which is not yet perfected, see a paper by A. Müller in *Zeitsch. analyt. Chem.*, 1863, 2, 143.

Acetate of Lead.

Principle. Ready solubility in water, and power of precipitating many acids. Compare, for example, Sulphate of Lead, Chromate of Lead, Phosphate of Lead, etc.

The best commercial acetate of lead is usually pure enough. For use, dissolve one part of the salt in ten parts of water acidulated with a few drops of acetic acid.

Acetate of Sodium (or of Potassium).

Principle. Easy decomposition of the salt by strong acids, and feeble solvent power of the acetic acid set free.

Applications. Substitution of acetic for chlorhydric, sulphuric, or nitric acid in strongly acid solutions. Compare, for example, the Acetates of Aluminum and of Iron, or Phosphate of Iron.

The commercial salt is usually pure enough; it should be free from empyreumatic matter. Dissolve one part of it in ten parts of water.

Acetate of Uranium.

Principle. Power of precipitating Arseniate of Uranium and Phosphate of Uranium.

To prepare the acetate, heat finely powdered pitch blende with dilute nitric acid, treat the filtrate with sulphuretted hydrogen to throw

down copper, lead and arsenic; filter again, evaporate the filtrate to dryness, and heat the residue strongly enough to decompose the nitrates of iron, cobalt and manganese. Boil the residue with water and again filter. Evaporate the filtrate to crystallize nitrate of uranium, purify the nitrate by recrystallization, and heat the crystals until a little of the sesquioxide of uranium is reduced. Dissolve the yellowish-red mass in warm acetic acid, filter and let the filtrate crystallize. Acetate of sesquioxide of uranium will crystallize out, while the nitrate of uranium, which escaped decomposition, remains dissolved in the mother liquor. Or, saturate a solution of protochloride of uranium with ammonia-water, and dissolve the precipitate in hot acetic acid.

A solution of acetate of uranium should give no precipitate when tested with sulphuretted hydrogen. But on the addition of carbonate of ammonium, a precipitate, soluble in an excess of the carbonate, should be produced.

Acidimetry.

A term applied to methods of estimating the amount of free acid in acid solutions.

Method A. By Specific Gravity. It has been found by experience that the specific gravity of a mixture of water and an acid is greater than that of pure water; that, as a general rule, the specific gravity of such mixtures increases with the proportion of acid contained in them, and that each particular mixture has a certain definite specific gravity peculiar to itself. Consequently, if the specific gravity corresponding to each and every per cent of any given acid be carefully determined, once for all, by experiments upon mixtures of pure acid and pure water, made expressly for the purpose, it will afterwards be easy to determine the proportion of that acid in any aqueous solution by taking the specific gravity of the latter and comparing the result with those of the standard experiments, provided only that no substance besides the acid in question be dissolved in the solution.

The relations between specific gravity and per cent of pure acid have been determined experimentally for solutions of all the more common acids, and the results of these experiments, expressed in numbers arranged in tabular form, will be found in most of the dictionaries of Chemistry. (See Dictionary of Solubilities.)

In testing the value of an acid mixture in this way, the Hydrometer is sufficiently accurate for most purposes. It is very commonly employed in the scientific laboratory as well as in the work-shop. The precautions to be noticed are, that the test must either be applied at the temperature to which the Standard Table refers, or the observation must be corrected for that temperature, and that the sample of acid tested must be free, or nearly free, from soluble contaminations. Since many of

the common acids are volatile, it is easy to detect the presence of nonvolatile impurities by evaporating a portion of the acid to dryness in a suitable dish. Of the acids in common use, acetic acid is the only one which cannot readily be tested with the hydrometer when pure. See Specific Gravity and Hydrometer in this work, or in almost any treatise on Chemical or Physical Manipulation.

Method B. By neutralization with an alkaline solution of determined strength. The principle upon which this method depends is that caustic alkalies and alkaline earths combine readily with free acids to form neutral salts, having no action upon litmus and certain other coloring matters, while the presence of the smallest excess of either acid or alkali is instantly made manifest by its action upon the coloring matter.

After a standard alkaline solution of definite strength has once been prepared, it is easy to determine the amount of acid in any weighed or measured sample of an acid solution by adding to it a few drops of a solution of litmus, and then pouring in the standard alkali until the red color of the litmus just changes to blue. The quantity of alkali required to effect this change being noted in each case, the quantity of acid contained in the sample is readily ascertained by calculation from the known value of the alkali.

The standard alkaline solution most commonly employed, is prepared from caustic soda; but a solution of caustic potash, or of caustic lime in sugar water, would do as well. Ammonia water is sometimes used, and so are solutions of carbonate of sodium, of borax, and of ammonio-sulphate of copper. — Instead of litmus, various other coloring matters may be employed to indicate the point of saturation. See, in particular, Cochineal, Logwood and Turmeric.

Standard Caustic Soda [or Standard Caustic Potash] is prepared through the intervention of a standard acid (see Alkalimetry) as follows:—Make a solution of caustic soda by boiling carbonate of sodium with hydrate of calcium in the usual way,¹ and dilute the clear caustic liquor until its specific gravity is about 1.06, corresponding to five per cent of hydrate of sodium. Measure off into a porcelain dish, or a beaker placed upon white paper, thirty c.c. of test acid (see Alkalimetry), and add to the liquid as much of a violet solution of litmus as may be necessary to give it a faint red tint. Fill a burette² with the solution of caustic soda, and pour the latter into the test acid until the red tint just changes to blue. Repeat the experiment with another portion of

¹ Or simply dissolve some caustic potash, such as surgeons use, in water, and boil the solution with enough slaked lime to decompose any carbonate of potassium which may be present.

² For descriptions of the various forms of this instrument and of Erdmann's float, used to ensure accuracy in reading, see the works on Chemical Manipulation.

the test acid, and if the two results agree, proceed to dilute the alkaline solution in the manner described under Alkalimetry (test sulphuric acid), so that each volume of it shall be capable of exactly neutralizing a volume of test acid. In case twenty-five c. c. of the soda solution were sufficient to neutralize the thirty c. c. of test acid, five c. c. of water would have to be added to every twenty-five c. c. of that soda solution to reduce it to the proper extent, or for every one thousand c. c. of the soda solution two hundred c. c. of water. When the standard solution is made of such strength that the alkali in one thousand c. c. of it will exactly neutralize an equivalent weight of any acid (expressed in grammes), it is called *normal*.

Normal solution of soda is well adapted for the ordinary operations of acidimetry, but whenever the quantity of acid to be neutralized is small, it is best to use comparatively dilute solutions of standard alkali. To this end the normal solution may be diluted five times, or ten times, with water. To prepare a "one-tenth normal" solution, for example, measure off fifty c. c. of the normal solution with a pipette, allow the liquid to flow into a half-litre flask, fill the latter with water to the mark, and shake the mixture thoroughly.

In order to keep the standard soda solution free from carbonic acid, the bottle which contains it may be provided with a cork carrying a bulb tube open at both ends, filled with soda-lime, so that air free from carbonic acid may pass into or out of the bottle, accordingly as the barometric pressure or temperature of the air changes. Sometimes it will be found convenient to provide a syphon tube through which the soda solution may be drawn off without need of opening the bottle. In this event a bent glass tube reaching nearly to the bottom of the bottle is fitted to the cork beside the bulb tube, and to the end of its outer limb, which reaches to a point below the bottle, is attached a short piece of caoutchouc tubing. After the syphon has once been filled, the caoutchouc tube is kept compressed with a spring clip, excepting at the moments when portions of the solution are allowed to flow out. In most cases, however, this syphon arrangement may be dispensed with.

Instead of taking pains to make the soda solution normal, as above described, it is often more convenient to choose a solution of soda of about the proper degree of concentration, as determined by the hydrometer; to determine its strength accurately by means of a standard acid, and then to use it directly as test alkali without any further preparation. This method of procedure of course necessitates a short calculation in each case, in order to obtain the percentage of acid.

It is convenient sometimes in technical analyses to have the number of cubic centimetres, or half cubic centimetres, of the standard al-

kali used, express directly the percentage of acid (either anhydrous or hydrated) in the sample tested. This may be accomplished by using normal alkali, and operating upon a weighed quantity of the acid to be tested equal to one-tenth or one twentieth of an equivalent weight of the acid sought for, expressed in grammes. The following table gives the number of grammes of each of the more common acids which must be taken in this event:—

Name of the acid.	No. of grms. equal to one-tenth of an equiv. wt. of the acid.	No. of grms. equal to one-twentieth of an equiv. wt. of the acid.
Anhydrous Acetic Acid,	5.1	2.55
Monohydrated " "	6.0	3.00
Chlorhydric Acid,	3.65	1.83
Anhydrous Nitric Acid,	5.4	2.70
Hydrated " "	6.3	3.15
Anhydrous Oxalic Acid,	3.6	1.80
Crystallized " "	6.3	3.15
Anhydrous Sulphuric Acid,	4.0	2.00
Monohydrated " "	4.9	2.45
Anhydrous Tartaric Acid,	6.6	3.30
Hydrated " "	7.5	3.75

Since the small quantities expressed in the above table could hardly be weighed out directly with sufficient accuracy, it is best to weigh out half equivalent weights (or in other words, five times as many grammes as are indicated in the first column of figures) of the acids, in a five hundred c. c. flask; to fill the flask with water to the mark, and after shaking its contents to measure out portions of the liquid with a pipette, for analysis. One hundred c. c. or fifty c. c. of the liquid must be taken, according as one-tenth or one-twentieth of an equivalent weight of the acid is to be used. In diluting the acid with water, care must be taken if need be, to cool the mixture before adding the last drops of water.

A Standard Solution of Lime in sugar water has the merit of being always free from carbonic acid, for in case the solution absorbs any carbonic acid from the air, insoluble carbonate of calcium is precipitated. To prepare the solution, add slaked lime to a cold, moderately strong, but not too strong solution of white sugar, as long as any of it will dissolve. Filter the solution, determine its strength by means of a standard acid, and dilute with as much water as may be needed. The solution of course becomes weaker in proportion as it absorbs carbonic acid from the air, though the deterioration is found to be very slow when the liquor is kept in tightly stoppered bottles. The strength of the solution must, on this account, be redetermined by means of standard acid at the beginning of any new series of determinations, or according to Gr. Williams (*Pharm. Journ. Trans.*, 1854, 13. 596), at intervals of four or five weeks. One advantage of the lime solution is found in the fact that acetate of calcium has less action upon the color of litmus than the acetates of sodium and

potassium. The lime solution is consequently well fitted for testing Acetic Acid.

Standard Solutions of Lime water and of Baryta water are used with advantage against oxalic acid and sulphuric acid for estimating Carbonic Acid. (After Dalton & Hadfield, and Pettenkofer). — Pasteur also (*Dingler's polytech. Jour.*, 190. 139 and *Zeitsch. analyt. Chem.*, 8. 86) employs lime water against sulphuric acid for determining the amount of acid in must (unfermented grape juice). For this purpose a dilute standard acid is prepared, of such strength that ten c. c. of it shall contain 0.06125 grm. of the monohydrate, and saturate about twenty-seven c. c. of lime water. This quantity of sulphuric acid is equivalent to 0.0725 grm. of anhydrous malic acid, to 0.09375 grm. of crystallized tartaric acid and to 0.2351 grm. of cream of tartar. Ten cubic centimetres of clear, filtered must are taken for an experiment, and the standardized lime water is poured into it from a burette graduated to tenths of cubic centimeters. Since must always contains substances which are colored by alkalies, it is not necessary to add any litmus to indicate the point of saturation. It is not well, for that matter, even to use litmus paper at the close of the operation, for malate and tartrate of calcium exhibit an acid reaction with litmus, just as the acetate does. (See Acetic Acid). The lime water should merely be added to the must, rapidly and without intermission, until the character of the color of the liquid changes, or in case the must be colorless at first, until the appearance of a tolerably pronounced yellow color. One or two drops should be subtracted from the amount of lime water actually used, in order to reduce the reading from the point of supersaturation to that of saturation.

As a rule, no precipitate of any kind falls at the moment when the color changes, but if the mixture be left at rest for a few minutes, or better, for a half hour or hour, it will become cloudy from deposition of granular crystals of normal tartrate of calcium, or more rarely, of a double compound of tartrate and malate of calcium, which contains one molecule of each salt plus sixteen molecules of water. These precipitates are easily distinguishable under the microscope. No harm is done in case the precipitate should form during the titration.

Whenever there is any difficulty in filtering a sample of must, a quantity of the standard lime water insufficient to effect complete saturation, may be added to a measured quantity of the muddy liquor—enough, for example, to make the liquid give a blue reaction upon sensitive red litmus paper; the solution may then be filtered, and lime water added, drop by drop, to ten c. c. of the clear filtrate, until the color changes. It is then easy to reckon how much lime water in all has been neutralized by acid in the must.

A standard solution of Ammonia-water is to be commended in certain cases, inasmuch as the strong liquor necessary for its preparation may be obtained ready made of every druggist. Were it not for the easy volatility of ammonia, and the consequent difficulty of keeping a standard solution of it unchanged for any great length of time, it would be often employed in acidimetry.

A standard solution of Carbonate of Sodium may readily be prepared by weighing out a convenient quantity of pure, anhydrous carbonate of sodium, and dissolving it in a determined quantity of water;—fifty-three grms. to the litre would be the proportion for a normal solution.

So far as mere preparation is concerned, a standard alkaline solution may evidently be obtained in this way more directly and with less risk of error than by the roundabout methods required in the case of the caustic alkalies. But since the reaction of carbonic acid upon litmus interferes with the reaction of the stronger acids and of the alkalies, a solution of carbonate of sodium is inferior—as a standard alkali—to a solution of caustic soda. It is seldom used in acidimetry, though sometimes employed in the preparation of standard acids, as will be explained under Alkalimetry. (See standard nitric acid). If a solution of cochineal be employed instead of litmus to indicate the point of saturation, the disturbing influence of carbonic acid is far less marked.

Instead of using a coloring matter as the indicator, the point of saturation may be determined by the precipitation of carbonate of barium, as follows:—Add a small quantity of a solution of chloride of barium to the acid to be tested, set the beaker which contains the mixture upon a black ground and pour into it a standard solution of carbonate of sodium, until a persistent cloudiness, due to precipitated carbonate of barium, pervades the liquor. — Acids which, like sulphuric acid, form insoluble compounds with barium, may be treated with a slight excess of chloride of barium, the mixture filtered to separate the insoluble barium salt, and the filtrate, or some definite fraction of it, may then be titrated with the standard carbonate of sodium (Mohr).

Standard solution of Biorate of Sodium. Like carbonate of sodium, borax is an excellent material for preparing a standard alkaline solution, inasmuch as any desired quantity of the dry or crystallized salt may be weighed directly upon the balance. A weighed quantity of borax has only to be dissolved in as much water as may have been determined upon, in order to complete the preparation of the standard solution. — The boracic acid set free when the borax solution is mixed with strong acids has far less action upon the color of litmus than is exerted by carbonic acid. Perfectly satisfactory results can in fact be obtained by titrating acids with the borax solu-

tion, even when nothing but litmus is employed to indicate the point of neutralization, especially if the solution to be tested be hot. But if a fresh decoction of Brazil wood be employed as the indicator, instead of litmus, the influence of boracic acid upon the final reaction becomes wholly inappreciable. The solution of Brazil wood should be prepared from clippings taken directly from solid blocks, not from the clippings which are to be found in commerce. The yellow Brazil wood solution is colored purple by alkalies, but becomes of a clearer yellow or reddish tint, when brought into contact with acids. (Stolba, *Journ. pratik. Chem.*, 1864, **90**, 459).

Since borax is rather sparingly soluble, it is impossible to employ a normal solution of it. Even a one-quarter normal solution, which would contain only 47.75 grms. to the litre, sometimes deposits crystals in cold weather. The use of borax solutions is consequently limited to those cases where only a dilute test alkali is needed. (Salzer, *Mohr's Titrimethode*, 1856, **2**, 102).

Standard Solution of Ammonio-Sulphate of Copper. Instead of using a standard solution of pure alkali to neutralize the acid which is to be estimated, and a solution of litmus or other coloring matter to indicate the point of saturation, it is quite possible to make a single solution serve both purposes. A solution of chloride of silver, for example, in ammonia water, or of oxide of zinc in potash, soda or ammonia, of alumina in potash or soda, or, best of all, of basic sulphate of copper in ammonia water, may be employed both to neutralize the acid, and to show when the neutralization is complete.

The solution of ammonio-sulphate of copper (first proposed by Kieffer, *Annal. der Chem. und Pharm.*, **93**, 386) is prepared by adding ammonia water to a tolerably strong, warm, aqueous solution of sulphate of copper, until the basic sulphate at first thrown down has almost completely dissolved; the liquid is then filtered, and its strength determined by titration with a standard acid, which may be either chlorhydric, nitric or sulphuric. Oxalic acid cannot be used in this case, since an insoluble oxalate of copper would be formed and the liquid obscured. When the ammonio-sulphate of copper is dropped into an acid solution, it neutralizes the free acid just as any other alkaline liquid would, but at the moment when all the acid is saturated the liquid suddenly becomes turbid from the deposition of a quantity of basic sulphate of copper. Though readily soluble in ammonia water and in acids, this sulphate is well nigh insoluble in neutral solutions. Hence that portion of it which was held dissolved in the final drop of the test liquor falls down when the ammonia is taken from it. Moreover, the last drop of the test liquor reacts not upon free acid, but upon sul-

phate, or some other neutral salt, of copper, which has been formed by the combination of a portion of the acid under examination with some of the copper in the test liquid. At the end, therefore, the ammonia in the test liquid combines with the acid of this neutral copper salt, and the copper contained in it is thrown down in the form of a subsalt at the same time with that from the test liquid, so that the volume of the precipitate is very considerable. The completion of the process is thus made distinctly manifest, for the appearance of the turbidity shows that the point of saturation has been reached.

The solution is brought to the required strength, and is employed for determining acids in precisely the same way as a soda solution, with the single exception that the point of saturation is indicated by the appearance of a precipitate instead of by a change of color, as when litmus or cochineal is employed.

This modification of the ordinary acidimetric process offers no special advantages in so far as relates to pure acids, excepting Acetic Acid, as already described, and is altogether inapplicable in the case of acids which form insoluble compounds with copper, such, for example, as oxalic, tartaric and phosphoric acids. It is peculiarly well adapted, on the other hand, for those cases where a free acid is mixed with any of the so-called acid salts. It may be employed, for example, to determine the free acid in the partially spent liquors—charged with sulphate of zinc—of galvanic batteries, or in the mother liquors resulting from the manufacture of sulphate of copper or sulphate of zinc.

Since the basic sulphate of copper is not absolutely insoluble in solutions of ammonium salts, the method is not to be commended in cases where strict accuracy is required. Carey Lea (*Amer. Journ. Sci.*, 1861, **31**, 190) has shown that the precipitate dissolves with considerable facility in a solution of sulphate of ammonium, that it is likewise soluble, though perhaps to a lesser degree, in solutions of chloride and of nitrate of ammonium, and that a larger or smaller quantity is held dissolved, according as the saline solution is more or less dilute. In practice, therefore, different results will be obtained from solutions containing precisely the same proportion of acid, in case they happen to be more or less highly charged with ammonium salts. Fresenius (*Zeitsch. analyt. Chem.*, **1**, 108), on the other hand, while admitting the justice of Lea's criticism, has shown by experiments that the errors likely to arise from this source are not of sufficient magnitude to condemn the process, in so far as relates to its applications for technical purposes.

It is to be observed that the acid solutions to be tested in this way must be clear; they should be placed in beakers set upon black paper. Since the copper solution is liable to lose am-

monia by standing, its strength should be redetermined from time to time, or before each new series of experiments.

The Actual Determination of the proportion of Acid may be performed as follows:—Weigh out in a small beaker or flask as much of the acid to be tested as will probably be sufficient to neutralize from 15 to 30 c. c. of the standard alkali, and add to it litmus enough to color the solution faint red. Fill a burette with the standard soda solution, and drop the latter rather quickly and without intermission into the acid, until the whole of the liquid in the beaker remains distinctly blue for some seconds. The acid must be stirred continually from first to last. After the point of neutralization has once been reached, no attention need be paid to the gradual reversion of the blue color to violet, caused by the action of carbonic acid from the air. — Note the quantity of standard soda solution which has been consumed, and proceed to calculate the proportion of acid. Suppose 4.5 grms. of dilute acetic acid were weighed out, and that 25 c. c. of normal soda solution, containing 40 grms. (= one molecule) of hydrate of sodium to the litre, were required to neutralize the acid, then the proportion

$$1000 : 25 :: 60 \left[= \frac{\text{Molecular wt. of } C_2H_3O_2}{\text{wt. of } C_2H_3O_2} \right] : x \left[= 1.5 = \frac{\text{Weight of } C_2H_3O_2}{\text{in sample taken.}} \right]$$

will indicate how many grammes of pure acetic acid were contained in the weighed quantity of dilute acid, and the proportion

$$4.5 : 1.5 = 100 : x [= 33.33]$$

will give the percentage of pure acid which the sample contained.

If the acid solution be kept hot while the standard soda solution is added to it, the point of saturation can be distinguished without difficulty, even when the soda solution is contaminated with some carbonic acid; but in cases where the operation has to be performed in the cold, as when the acid under examination is volatile, or mixed with ammonium salts, the caustic soda employed should be free, or nearly free from carbonate. No matter how pure the soda, the change of coloration is more readily recognized in hot than in cold solutions. In any event the change of color of the litmus from red to blue is less clearly defined with weak acids, such as most of the organic acids, than with strong acids, such as sulphuric, chlorhydric, nitric, and the like. The blue tint, indicative of the point of saturation, may be obscured also, or modified, by the presence of various substances. If the acid solution contains ammonium salts, for example, the change of color from red to blue is less quick and decided than when they are absent. In all cases of doubt, and particularly when a color peculiar to the liquid obscures the color of the dissolved litmus, it is best to determine the point of neutralization by placing successive drops of the liquid upon litmus paper, in the

manner described under Acetic Acid. It is to be observed, however, that in determining the point of saturation with litmus paper, a little more alkali will almost always be used than would be the case if the litmus were in solution. In very delicate experiments it may sometimes be worth while to determine the amount of this excess, and to allow for it in estimating the acid. This may be done by measuring off a volume of water equal to that of the acid tested, and adding to it drops of the soda solution until the reaction of the liquid upon litmus paper is just as strong as that previously exhibited by the liquid, which contained the acid. The quantity of alkali required to effect this result is then subtracted from the quantity actually employed in neutralizing the acid.

See Alkalimetry for the method of using cochineal instead of litmus. See also Cochineal and Logwood.

Estimation of Combined Acids. Though the term acidimetry is commonly understood to apply only to the estimation of free acids in simple solutions, or in solutions charged with substances having no action on alkalis, the process may nevertheless be extended in some instances to the determination of acids combined with metals. — A description of one method of this character, as applied to the estimation of acetic acid when combined with copper, iron, and other metals precipitable as hydrates, oxides or carbonates, by caustic or carbonated soda, has been given already under Acetic Acid.

Another general method of determining the amount of acid in a compound—based upon the insolubility of various metallic sulphides—should here be mentioned. This method is applicable to the estimation of non-volatile acids, which are not acted upon by sulphuretted hydrogen when combined, to form compounds soluble in water, with any metal which can be easily and completely precipitated by sulphuretted hydrogen. The process is as follows:—Weigh out a quantity of the salt to be analyzed, dissolve it in water, boil the solution, and pass a stream of sulphuretted hydrogen through the liquid until the metal is completely precipitated. In order to determine when the precipitation is complete, take out drops of the clear liquid from time to time upon a glass rod, place them upon porcelain, and add a drop of strong sulphuretted hydrogen water, or of any other reagent specially adapted for testing the metal in question. When quantities of salts as large as 5 grammes are operated upon the precipitation is usually complete in half an hour. When all the metal has been thrown down, filter the liquid rapidly, wash the precipitate with hot water until the washings no longer exhibit an acid reaction, and collect the filtrate and wash water in a half litre or a litre flask. Cool the liquid and dilute it with water to the volume of half a litre, or a litre. Agi-

tate the mixture thoroughly, take out with a pipette several portions of 50 or 100 c. c. each, and place them in separate beakers, add a few drops of cochineal or logwood to each of the solutions, and determine the amount of free acid in each with dilute standard alkali in the usual way. As the standard alkali, Gibbs employs one-tenth normal ammonia water. The results of the 1st determination should be regarded as merely approximative, and the mean of the 2d and 3d (or of several successive) determinations taken as the true result. From the quantity of standard alkali used, not only the quantity of acid in the salt examined, but, in many cases, that of the metal also, may be readily calculated.

The precipitation of a metal by sulphuretted hydrogen from boiling solutions is usually comparatively slow, but the boiling is nevertheless necessary in order that the filtered liquid may contain no sulphydric acid. — In operating upon nitrates and chlorides, a quantity of some neutral salt of a fixed organic acid must be added to the solution before passing the sulphuretted hydrogen. A quantity of the organic acid equivalent to that of the mineral acid is then set free, so that none of the mineral acid is lost through volatilization, and none of the nitric acid destroyed by the hot sulphuretted hydrogen. A quantity of Rochelle salt about equal to the quantity of the salt taken to be analyzed, may be used for this purpose.

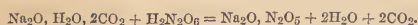
The process is inapplicable in presence even of very small quantities of iron, aluminum, and various other metals, which, with cochineal and logwood, give reactions not easily to be distinguished from those produced by the caustic alkalies. (Rose, *Pogg. Annal.*, 116. 125; Gibbs, *Amer. Journ. Sci.*, 1867 [2] 44. 207).

Principle II. Power of acids to expel carbonic acid from metallic carbonates.

Method. Mix a weighed or measured quantity of the acid to be examined with an excess of bicarbonate of sodium in an appropriate apparatus (see Carbonic Acid), and determine how much carbonic acid is expelled, either by weighing the apparatus before and after the experiment, and calling the loss of weight carbonic acid, or by absorbing the gas in soda-lime and weighing it directly. (See Carbonic Acid). The amount of free acid in the sample tested is then found by the proportion:

$$\frac{\text{Molecular wt. of } \text{CO}_2}{\text{Equivalent wt. of acid tested.}} = \frac{\text{Weight of } \text{CO}_2 \text{ found}}{\text{Weight of acid in sample.}}$$

It will be observed that 2 molecules of CO_2 are set free for every equivalent of acid in the solution:—



Enough acid should be taken to set free one or two grammes of carbonic acid. — The process affords satisfactory results, and may be employed with advantage in testing liquids so

highly colored that the ordinary method of acidimetry cannot be applied to them.

Aconitin.

See Iodomercureate of Aconitin.

Albumin.

Principle I. Coagulability by heat.

Applications. Estimation of albumin in alkaline solutions, such as urine and the serum of blood.

Method A. Acidulate the solution slightly with acetic acid and boil for several minutes. Collect the precipitate on a tared filter, wash thoroughly with warm water and dry in a current of warm air at 110° or 115° , or better, in vacuo, over sulphuric acid, until the mass ceases to lose weight. Care must be taken that the precipitate is thoroughly dried, for as soon as the moisture has been driven from its surface the mass acquires the consistence of horn, and forcibly retains the last portions of the water. The addition of acetic acid to the liquid is essential in order that the albumin shall be precipitated completely; but no great excess of the acid should be employed lest some of the albumin be dissolved by it. The precipitate thrown down from solutions thus acidulated is more flocculent and less apt to clog the pores of the filter during the process of washing than that obtained without the addition of an acid. — To determine albumin in urine, place 50 to 100 c. c. of the clear urine, previously filtered, if need be, in a flask large enough to hold twice as much of the liquid. Heat the liquor gradually, with frequent shaking until the albumin begins to coagulate, at about 70° , then throw a couple of drops of acetic acid into the flask from the end of a glass rod, and boil the liquor as above described (Neubauer & Vogel).

Method B. Another method of estimating albumin in urine, devised by Heller (*Heller's Archiv für Chem. und Microsc.*, 1852, p. 266 *et seq.*), is said to afford very accurate results in spite of being indirect:—Evaporate 10 or 15 grms. of the urine to dryness over sulphuric acid, and weigh the residue. Weigh out another quantity of the same urine in a small flask, acidulate it slightly with acetic acid, boil until all the albumin is precipitated, and after the liquid has become cold place the flask upon the balance and add to it, drop by drop, water enough to replace what has evaporated. Filter the contents of the flask and evaporate a weighed portion of the filtrate to dryness over sulphuric acid. The difference between the percentage of residue left by the original urine and that obtained from the urine after the separation of the albumin gives the proportion of the latter ingredient.

Method C. For comparing the quantities of albumin in any two different samples of urine, Dr. John Harley has adopted the following process:—Make 3 small filters from the same sheet of paper, cut down the two heavier to the weight of the lightest, and mark the filters

with a pencil, A, B, and O. Take 1000 grain measures of urine A, and having boiled it, pour it while hot upon filter A. Treat urine B in a similar way. Wash the contents of each of the filters with warm water until the last traces of adhering urine have been removed. Then pour upon the albumin an ounce of water containing 2 drops of nitric acid, and subsequently wash out the acid with water. The filter marked O is placed in the first instance between one of the other filters and the funnel, and is thus equally saturated with urine and acid, and equally washed free from both. All 3 filters are dried together, and the empty filter is used as a counterpoise in determining the weight of the albumin upon the others.

Properties. Albumin, as it occurs in the state of solution in the animal economy, is combined not only with water but with minute quantities of certain saline and alkaline ingredients. When a solution of pure albumin is evaporated in vacuo, at temperatures below 50° , there is left a light yellow, translucent mass of soluble albumin, which may be readily rubbed to a fine white powder. When treated with water, this residue swells up to a jelly, without, however, dissolving to any very considerable extent, unless a small quantity of an alkaline salt be present. By the action of most mineral acids, and of many other chemical agents—sometimes by mere contact with atmospheric air, this soluble modification of albumin is changed to the coagulated, insoluble condition.

Insoluble albumin, when recently precipitated and still moist, is a tough, white, opaque, floeculent solid, insoluble in water, alcohol, ether, and most acids when dilute and cold. When left moist in the air it putrefies. It is somewhat soluble in hot acetic, tartaric, phosphoric, and strong chlorhydric acids. When boiled for a long time with water it decomposes and dissolves. On being dried it assumes a yellow color and becomes brittle and translucent like horn. When soaked in water, after drying, it takes up about five times its weight of the liquid and becomes soft and elastic.

Principle II. Opacity.

Applications. Estimation of albumin in aqueous and saline solutions.

Method. Prepare a little trough of sheet iron with glass ends, as follows:—Provide three rectangular sheets of metal, one 7 e. m. square, the others 4 e. m. long by 2.5 e. m. wide. Bend the square sheet into the form of a V-shaped gutter, the upper edges of which are 1 e. m. apart. From each of the smaller sheets cut out wedged-shaped pieces of metal, corresponding to the shape of the trough, so that when the sheets are placed in an upright position, the V-shaped trough may fit into the cuts and be supported as by feet. Place one of these supports near each end of the trough and solder them to the trough. Cut out two V-shaped pieces of window glass, fitted to the

trough, and cement them into the ends of the trough with Canada balsam, taking care to place the glasses parallel to one another, and to leave a clear distance of 6.5 e. m. between them. The glasses can be cemented the more readily in case a notch or groove be made upon the iron in the beginning to receive them. The metal of the trough should be painted with asphaltum varnish to protect it from rust.

As applied to the estimation of albumin in urine, the process of testing is as follows:—Filter the urine, in case it is not clear, acidulate it slightly with acetic acid, if it be not already acid, and proceed to determine how much the urine must be diluted to fit it for the test. To this end prepare several dilute solutions by mixing measured portions of the urine with water and boil each of the solutions in regular order, until one is found in which the albumin no longer separates in distinct flocks, but only as a milky cloud. It is a liquid thus clouded by the presence of fine particles of suspended albumin, which admits of being subjected to the test of opacity. — The best way of preparing these dilute solutions is the following:—By means of a little pipette graduated to 0.1 e. c., take up 6 e. c. of the urine and transfer it to a 100 e. c. flask. Fill the flask with water to the mark, shake the mixture thoroughly, pour the liquid into a beaker and leave the flask inverted in order that it may drain. Meanwhile pour 6 or 8 e. c. of the diluted urine into a test tube of 20 or 25 e. c. capacity, heat the liquid to boiling, and afterwards cool it quickly by immersing the tube in cold water. In case the precipitate produced by boiling is so slight that the form of objects placed in strong daylight can be distinguished on looking at them through the liquid, the sample has been too much diluted, and the operator will at once proceed to prepare a more concentrated solution by mixing 12 e. c. of the original urine with water in the 100 e. c. flask. But in case the first solution was not transparent, it may be tested in the trough. — In testing, fill the trough two-thirds full of the cold, boiled liquid, and look through the liquid at the flame of a burning candle in a darkened room. Repeat the experiment with other diluted samples of the urine until a point is reached where the shape of the flame cannot be distinguished, and only diffused light can be seen through the liquid, even when the candle is brought close to the trough. — In case the flame is visible through the first solution, the next trial must be made with a solution containing a few more per cents of urine than the first. But if the shape of the flame cannot be distinguished, the liquor of the subsequent trial must be more dilute, and so on methodically, until a liquid is obtained, through which the reddish yellow cone of flame can only be seen by looking with the strictest attention, as if it were in a thick

fog. When this point is reached it is only necessary to add a trace more urine (0.1 or 0.2 per cent) in preparing the next diluted sample, in order that the flame may become completely invisible, and the operation be finished. — To find the percentage of albumin, divide the number 2.3553 by the number of c. c. of urine taken to prepare the dilute solution through which the flame could no longer be seen. This number, 2.3553, is the mean of 35 experiments by Dragendorff, in which the results of the optical test were controlled by precipitating and weighing the albumin.

Precautions. In looking at the flame, the trough should be held before the eye like a spy-glass, and moved forwards and backwards from a distance of 0.5 metre from the candle close up to the flame, while the instrument itself is continually pressed lightly against the eyebrow. Up to a certain point the last glimpses of the cone of flame can be seen more readily, in proportion as the trough is closer to the candle, but if the flame is too near the liquid, the latter is illuminated by a reddish yellow light, through which the flame is seen less readily. The chamber in which the operation is conducted, should always be dark enough that the yellow light of the candle may overpower the daylight.

In case albumin separates from a diluted liquor in small flocks, the liquor may often be made cloudy and fit to be tested by shaking it violently as soon as the flocks appear. Densely clouded liquids, on the other hand, may be used for preliminary, approximative tests, by mixing them with measured quantities of water. But the results of such experiments must always be controlled by testing samples of urine which have been diluted before boiling. Better results can always be obtained by boiling weak solutions of albumin than by boiling comparatively strong solutions and mixing the cloudy liquor with water. — Instead of the 100 c. c. flask above prescribed, a 50 c. c. flask may be used, but rather more accurate results can be obtained when the larger volume of liquid is operated upon. The pipette employed must be graduated to 0.1 c. c., so that quantities of liquid as small as 0.05 can be measured with it.

The chief difficulty of the process is found in endeavoring to properly acidulate the original urine. Many samples of albuminous urine yield no precipitate, or only a comparatively feeble precipitate on boiling, when too strongly acidulated with acetic acid, and, in like manner, less albumin is obtained by the optical test than by the method of precipitation, in case the acid reaction of the urine is indistinct. It is important that the urine should be kept in a cool place in order that it may be as fresh as possible when tested. — The original urine need not be filtered unless it contains a distinct precipitate. Urine that is merely cloudy will usually become clear when mixed

with much water. Some samples of albuminous urine, however, become cloudy when treated with a few drops of acetic acid, or with 5 or 10 times their volume of pure water, and it is precisely this kind of urine which is least readily tested by the optical method. Special care must be exercised in adding acid to such urine, since the presence of a trace of acetic acid in excess may present the appearance of any precipitate on boiling. The cloudy solution (paralbumin) produced on mixing the urine with water, need not be filtered. The mixture should be boiled at once, as if it were clear. — The process is easy of execution, and is said to yield very accurate results, excepting perhaps those kinds of urine which become cloudy on the addition of acetic acid. Ordinarily no more than 5 or 6 of the diluted samples of liquid have to be tested in order to hit the point of obscuration; so that the determination will be finished in the course of half an hour. — The several experiments of the series above mentioned agreed with one another in most instances to the second decimal place. Only 3 experiments out of the 35 differed more than 0.1, and only 11 more than 0.05, so that 21 of the trials agreed to 0.05 per cent. (Alfred Vogel, *Zeitsch. analyt. Chem.*, 1868, 7. 152).

Principle III. Power of rotating the plane of vibration of a ray of polarized light.

Applications. Estimation of albumin in aqueous or saline solutions, such as urine and the serum of blood.

Method. When a ray of polarized light is made to pass through a column of albumin solution enclosed in a tube, it is found that the plane of polarization is rotated to the left, and that the angle of deviation is proportional to the length of the column of liquid. In like manner, when a tube of any given length is successively filled with solutions containing different quantities of albumin, the angle of deviation is found to be proportional to the amount of albumin in the liquid.

An apparatus, known as Soleil's Albuminimeter, used for measuring the rotatory power of albumin, resembles the ordinary Saccharimeter (see Sugar), with the exception that in place of the Nicol's prism there used as the analyzer, a double refracting prism is employed, cut in such manner that only a single image shall appear in the field of vision. An intense white light, such, for example, as that of a petroleum lamp, is needed. The lamp is placed in a blackened box provided with a reflector which throws the rays of light upon a moveable lens by which they are concentrated before reaching the apparatus.

After the lamp has been lighted and placed in front of the apparatus, put a piece of red glass in front of the polarizing prism in the path of the luminous rays, and turn the analyzing prism until the luminous image has completely disappeared. The zero point of

the apparatus having thus been determined, fill the tube with the solution to be tested, place it in the apparatus and leave the liquid at rest during some minutes. On again looking into the apparatus it will be seen that by virtue of the rotatory power of the liquid in the tube, the luminous ray has again become visible, and it will be found that the index of the apparatus must be turned through a certain number of degrees in order to again extinguish the ray. But by counting the number of degrees and minutes between the two points of extinction, it is easy to determine the amount of the rotation and to estimate therefrom the proportion of albumin in the liquor. — It is important to exclude external light as completely as possible; to make several observations with each sample of liquid, and to read the divisions of the circle and vernier carefully; best with a good lens.

In case serum of blood is to be tested, about 1 grm. of sulphate of sodium should be added to each 100 grms. of the liquid, and the mixture filtered immediately, in order to separate blood globules and other suspended particles. The purpose of the sulphate is merely to facilitate the filtration; in the case of urine none of it need be added. The yellowish orange color exhibited by serum when viewed in thin layers, becomes distinctly red when seen in a long column like that in the tube of the albuminometer. In general, however, this coloration is not intense enough to do any harm; it simply obviates the need of using the red glass, for, like the latter, it only permits the passage of red rays.

In a series of 50 experiments upon blood serum, Becquerel found that the deviation of the plane of polarization varied between $4^{\circ} 30'$ and 9° , or on the average $7^{\circ} 30'$. In general, the deviation oscillated between 7° and 8° . The corresponding quantities of pure dry albumin were from 4.86 to 9.44 per cent. From these and like observations, it has been calculated that with a column of liquid 20 c. m. long, each minute of deviation corresponds to 0.18 grm. of albumin. (Becquerel, in *Robin & Verdeil's Chimie Anatomique*, 1853, 3. 316).

Principle IV. Specific Gravity.

Applications. Estimation of albumin in urine.

Method. Take the specific gravity of the urine and note the temperature of the liquid when the observation is made. Acidulate a quantity of the urine with acetic acid, place the liquid in a flask provided with a perforated cork carrying a vertical glass tube, and boil it until all the albumin has separated in the insoluble state. Cool the boiled urine to the temperature at which the specific gravity of the original urine was determined, and take the specific gravity of the clear filtrate. Multiply the difference between the two specific gravities by 210, in order to obtain the percentage of albumin in the sample. In a series

of 13 experiments, the least error was 0.005, and the greatest 0.056. (Lang, and Haebler, *Zeitsch. analyt. Chem.*, 1868, 7. pp. 513, 514).

An article on the estimation of albumin, by graminetric and volumetric methods, has been published by C. Boedeker, in *Henle & Pfeuffer's Zeitschrift für rationelle Medicin, Zurich*, 1859, 5. 320.

Alcohol.

Principle I. Solvent power.

Applications. Alcohol is used for separating many substances which dissolve in it from others which are insoluble, as when chloride of strontium is removed from chloride of barium; or precipitates, such as the sulphate or malate of calcium, are washed clean by means of it.

Two kinds of alcohol are commonly used in analysis, namely; "Spirit," or ordinary alcohol of 0.83 or 0.84 specific gravity (= 88 or 90 per cent by volume), and "Absolute Alcohol." The latter should be at least as strong as 0.81 specific gravity (= 96 or 97 per cent by volume). To prepare it mix a quantity of ordinary alcohol in a capacious flask or retort, with something more than its own volume of quick-lime, in small pieces. After the lime has slaked, leave the mixture to itself for several hours, and finally distil it slowly upon a water-bath.

Principle II. Reducing power.

Applications. Reduction of chromic acid to sesquioxide of chromium, of binoxide to protoxide of lead, etc.

Method. See, for example, Hydrate of Chromium.

Principle III. Volatility.

Applications. Separation of alcohol from aqueous solutions of non-volatile substances, as a preliminary to the determination of the strength of wines and spirit.

Method. As will appear from the article Alcoholometry, the value of spirits is usually determined by means of the Hydrometer. But since this instrument cannot be employed in case the spirit contain other soluble substances besides water, the alcohol, together with a part of the water, is first separated by distillation before the hydrometer is applied.

A measured volume of the liquid to be tested is placed in a glass flask provided with a cork and delivery tube, connected with a worm, or with a Liebig's condenser. Most of the liquid is then distilled over, the distillate carefully measured, and the proportion of alcohol contained in it is determined with the hydrometer. The amount of alcohol thus found must of course be referred to the volume of liquid originally placed in the flask or still.

Both the liquid to be distilled and the distillate must be brought to some common temperature before measuring, best by immersing the vessels which contain them in flowing water. The joints of the distillatory apparatus must be tightly fitted. In case the sub-

stance to be tested contains any free acetic acid or other volatile acid, neutralize it with caustic soda before distilling.

Alcoholometry.¹

A term applied to methods of estimating the proportion of alcohol in any spirituous liquid.

Method A. By Specific Gravity. See Specific Gravity and Hydrometer. Compare what is said of specific gravity under Acidimetry.

Applications. Determination of the proportion of alcohol in any mixture of alcohol and pure water. This method is convenient, accurate and rapidly executed. It is far more frequently employed than either of the other methods of testing alcohol. It would always be employed for practical purposes, were it not that the presence of sugar, salts, coloring matters, etc., in spirit, sometimes precludes its use.

To estimate alcohol by this method, even in presence of sugar, Zenneck, and after him Aug. Vogel, *Zeitsch. analyt. Chem.*, **6**, 273, proceeds as follows:—Carefully determine, in the first place, the specific gravity of the saccharine spirit at 15° upon a balance. Then weigh out about 150 c. c. of the liquor in a tared flask, and boil to expel alcohol, until about half of the liquid has evaporated. Remove the flask from the lamp, place it upon a balance, and pour in water until the weight of the flask and contents is the same as before boiling. Cool the aqueous solution of sugar to 15°, and determine its specific gravity. Look up in the published tables (*Dict. Sols.*, Art. Sugar) the percentage of Sugar, *S*, which corresponds to the observed specific gravity; $100 - S (=A)$ will then represent the percentage of mixed water and alcohol in the liquor under examination. The specific gravity of this plain spirit may be found by the formula:

$$x = \frac{1.606 \times D \times A}{160.6 - D \times S},$$

in which *D* = the specific gravity of the original mixture of sugar and spirit. When the specific gravity of the plain spirit is known, it is easy to obtain its percentage composition by referring to the published tables (*Dict. Sols.*, Art. Alcohol), and from the composition of the plain spirit, that of the original saccharine liquor may be easily calculated. — The formula above given is obtained as follows:—The specific gravity of cane sugar being 1.606, and that of the original saccharine liquor *D*, let *x* represent the specific gravity of the plain spirit. The volume of the plain spirit will be $\frac{A}{x}$ and that of the percentage of sugar $\frac{S}{1.606}$; hence

$$\text{Sp. gr. of the mixture} : D = 100 : \left(\frac{A}{x} + \frac{S}{1.606} \right)$$

and

$$x = \frac{1.606 \times D \times A}{160.6 - D \times S}.$$

¹ For the details of Alcoholometry, see *Handwoerterbuch der Chemie*, Braunschweig, 1856, 1, 493. Or almost any of the large Dictionaries of Chemistry.

In case the liquor contains no cane sugar, but only grape sugar, the number 1.39 (= specific gravity of grape sugar) must be substituted for 1.606 in the formula.

A prominent advantage of the process is found in the fact that only a comparatively small quantity of liquid is required for an experiment.

Method B. By determining the boiling point of the mixture, and comparing the result with the results of previous experiments made with standard liquids of known composition specially prepared by mixing pure alcohol and pure water. Tables of the relations of boiling points to per cents of alcohol will be found in most dictionaries of general chemistry. (See, for example, *Dictionary Solubilities*, Art. Alcohol).

Applications. Determination of the proportion of alcohol in mixtures of alcohol and water, and in fermented liquors as well. For mixtures of alcohol and pure water the method is inferior to Method A (by specific gravity). It finds useful application, however, in testing wines and beers, since it has been found that the foreign substances, other than alcohol and water, in fermented liquors, have little influence upon the boiling point of the mixed alcohol and water. Enough sugar or common salt may be added to spirit of 20 per cent, by volume, to reduce the liquor to 0° of Gay-Lussac's alcoholometer without altering the boiling point of the spirit to any appreciable extent. Several forms of Ebullioscopes have been invented for testing wine and beer. For a report upon the various forms of this instrument, see Despretz and others, *Comptes Rendus*, **27**, 374. A recent form of ebullioscope, by Brossard-Vidal, is described in *Zeitsch. analyt. Chem.*, 1864, **3**, 223. Wagner, in his *Jahresbericht chem. Tech.* 1863, **9**, 545, specially commends the ebullioscope of Tabarié. Ebullioscopes are much used for testing wine and beer, and the results obtained by them compare very favorably with those obtained by the method of distillation. (See under Alcohol). — In boiling beer it is well to add to the liquid a trace of tannic acid to prevent frothing.

Method C. By determining the Tension of the Vapor. An instrument called a Vaporimeter has been constructed by Geissler for this purpose. It consists of a vessel provided with a syphon tube, fitted by grinding to an orifice at its top. It is employed as follows:—Metallic mercury is poured into the vessel up to a certain mark, and the space above the mercury filled with the spirit to be tested; the syphon tube is then put in place, and the whole apparatus turned upside down. The quicksilver immediately falls into the bent tube and closes the spirit against contact with the air. The apparatus is then placed in an atmosphere of steam, in the upper part of a vessel in which water is boiling, so that vapor may be evolved from the spirit. The pressure exerted by the

alcohol vapor, forces a portion of the mercury to rise into the syphon tube, and from the height of this column of mercury, corrected for the atmospheric pressure at the moment of observation, the tension of the vapor is determined. The apparatus is usually provided with an empirical scale, which indicates the proportion of spirit in terms of per cent by volume.

Applications. Determination of the proportion of alcohol in solutions charged with sugar. It has been found that with solutions containing salts, such as chloride of sodium, the tension of the vapor evolved at any given temperature is greater than it would be for a mixture of alcohol and pure water. But sugar exerts no influence. In case the saccharine spirit to be tested contains carbonic acid, or any other volatile acid, the liquid must be saturated with lime before placing it in the vaporimeter. The method is of course one of technical, rather than of scientific, application.

Method D. By Determining the Rate of Expansion of the Liquid by Heat. Instruments have been constructed for this purpose by Silbermann (*Comptes Rendus*, 27. 418) and by Makins (*Journal of Chemical Soc.*, London, 2. 224). Silbermann's Dilatometer consists of a thermometer tube, which is filled up to a certain mark with the spirit to be tested, at the temperature of 25°. The air which the liquid holds dissolved is then removed by means of an air pump, and the tube and spirit finally exposed to a temperature of 50°. The amount of expansion is observed, and the proportion of alcohol in the sample found by referring to a scale previously graduated by direct observations upon samples of spirit of known strength.

Applications. The instrument can be used with mixtures containing sugar or salt, since these substances have been found to exert little or no influence on the expansibility of spirit.

Method E. By Capillary Attraction. The instrument known as a Liqueometer, in which the determination is made, consists of a capillary glass tube 4 inches long, graduated to 20 degrees, and fitted to a hole in the cover of a glass vessel so that it can be elevated or depressed in the vessel. After the glass vessel has been three quarters filled with the spirit to be tested, the capillary tube is pushed down so that about 0.1 inch of the lower end of the tube shall be immersed in the liquid; a quantity of the spirit is drawn up into the tube by sucking at the upper end to moisten its walls, and the tube again drawn up carefully until its lower end is precisely level with the surface of the spirit. Again suck carefully at the top of the tube, so that the liquid may rise in the tube, and afterwards note the point at which the liquid remains stationary when it is allowed to sink back towards the glass vessel. Compare the degree at which the spirit stands in

the tube with the published tables, in order to obtain the percentage of alcohol. (Reynolds, *London Pharm. Journ. and Trans.*, [2.] 9. 171, and *Zeitsch. analyt. Chem.*, 1868, 7. 358).

Method F. By Ultimate Analysis. A weighed portion of any mixture of alcohol and pure water could be burned by means of an oxidizing agent (see Carbon), the resulting carbonic acid weighed, and the quantity of alcohol computed from these data. But the method would only be of scientific interest. It has no practical application.

Alkalimetry.

A term applied to the estimation of free alkalies and alkaline carbonates.

Method A. By Specific Gravity. In pure or nearly pure solutions of ammonia, or of the hydrates of sodium and potassium, the proportion of alkali may be inferred with tolerable accuracy from the specific gravity of the solution. (See Acidimetry). But the method is of less general applicability with alkalies than with acids, since, with the exception of ammonia-water, alkaline solutions are rarely found pure.

Method B. By neutralization with an acid solution of determined strength. This method is the precise opposite of the method of Acidimetry by saturation, already described. It consists in determining how much acid of known strength is required to neutralize a definite weight of the sample of alkali under examination.

The chief requisite in this process is of course the *standard or test acid*; which may be made either from sulphuric, oxalic, chlorhydric or nitric acid, according to circumstances.

Standard acid may be prepared either by dissolving a definite weight of a crystallized acid, such as oxalic acid, in water, in such manner that each c. c. of the solution shall contain a certain proportion of the dry acid; or by adding the requisite proportion of water to any moderately dilute solution of sulphuric, chlorhydric, or nitric acid, after the proportion of real acid in that particular sample has been determined by analysis or by titration. The details of the several methods will be given below.

Standard acid is often made of such strength that a litre (= 1000 c. c.) of it shall contain exactly one equivalent of the dry acid, expressed in terms of grammes; it is then called "*normal acid*." Thus normal chlorhydric acid should contain 36.5 grms. of HCl to the litre, and normal sulphuric acid 40 grammes of SO₃. Equal volumes of different normal acids have of course the same power of saturating alkalies. Sometimes the test acid is made to contain only a fraction of the quantity of real acid which would be required if it were normal. Thus an acid containing 7.3 grms. HCl to the litre, is called "*one-fifth normal*," while one that contains 3.65 grms. is "*one-*"

tenth normal." Several methods of preparing standard acids will be set forth in the following paragraphs.

Standard Sulphuric Acid.

A. Normal Sulphuric Acid. Counterpoise a small flask or beaker with shot or sand upon a rough balance, and weigh out in it 60 grms. of concentrated sulphuric acid. Put 1050 c. c. of water in a large flask and pour the acid into the water while shaking the flask. After the mixture has become cold, pour a part of it into a burette, measure off into beakers two portions, of about 20 c. c. each, of the liquid, and determine the quantity of sulphuric acid in each portion by precipitating it as Sulphate of Barium. If the results of these determinations are concordant, take the mean of the two as representing the amount of acid actually contained in the mixture. Pour the rest of the acid solution into a graduated mixing cylinder, note its volume and pour in as much water as may be required to dilute the liquid to the condition of normal acid (i. e., 40 grms. to the litre). If it were found, for example, that the 20 c. c. of liquid tested contained 0.84 grm. of sulphuric acid, then 1000 c. c. would contain 42 grms., and to every 1000 c. c. of the solution 50 c. c. of water would have to be added, for

$$40 : 1000 = 42 : x (= 1050).$$

In default of a mixing cylinder, the dilution may be effected in a litre-flask, as follows:— Fill the flask up to the mark upon its neck with the acid mixture to be diluted, so that the lower edge of the curved depression at the top of the liquor shall coincide with the line upon the glass; empty the liquid carefully into a large stoppered bottle; measure off with a pipette or burette the amount of water required for the dilution; transfer this water to the flask from which the acid has just been poured; shake the flask thoroughly, and add its contents to those of the bottle; shake the bottle thoroughly, pour back half its contents into the litre-flask, agitate the latter, pour back the liquid from the flask into the bottle, again shake the bottle and keep its contents for use.

As is the case with all standard solutions, the bottle should always be shaken just before any portion of its contents are to be poured out for use, unless indeed it be absolutely full of liquid. For when a bottle is but partly filled with a solution, some water is apt to evaporate into the space above the liquid and condense there upon the glass in such manner that if a small portion of liquid was to be poured out of the bottle without shaking, it would wash off the condensed water and become slightly diluted, while the liquid remaining in the bottle would be left a trifle stronger after each pouring.

Instead of determining the sulphuric acid by precipitating it as sulphate of barium, the proportion of acid in the sample chosen may

be discovered by noting how much of this acid is required to neutralize a given weight of pure carbonate of sodium. The determination may be made either in the manner described in § *a*, or, more accurately, by that set forth in § *β*. It is to be observed, as a general rule, that a standard acid is best prepared by the same method as that for which it is to be subsequently used. If sulphuric acid, for example, is to be used for testing the value of commercial carbonate of sodium, it should be standardized against pure carbonate of sodium by the very method which is afterwards to be applied in testing the commercial carbonate.

α. Weigh out (best from the covered platinum crucible in which it has been ignited) from 4.5 to 5 grms. of pure, anhydrous carbonate of sodium. Place the salt in a capacious flask or porcelain dish, dissolve it in about 200 c. c. of hot water, and color the solution blue with 1 or 2 c. c. of a solution of litmus (or, instead of litmus, color the cold solution with Cochineal, or with Logwood). — Mix about 60 grms. of ordinary, monohydrated sulphuric acid with 500 c. c. of water, allow the solution to cool, and fill a burette with the cold dilute mixture. Stir the solution of carbonate of sodium with a fine glass rod, and gradually pour into it, from the burette, the cold dilute acid, until the color of the solution changes to a wine red; then place the flask or dish over a lamp and heat its contents to boiling. The wine red coloration is caused by the action of carbonic acid which has been set free, and the liquid is heated in order to drive out this volatile acid. As soon as the color of the liquid has become blue again pour more sulphuric acid from the burette into the nearly boiling liquid, until the solution assumes the peculiar deep red color, slightly inclined to orange, which is characteristic of the strong acids.

Since, in liquids thus charged with carbonic acid it is not easy to determine when the operation is finished, if the color of the dissolved litmus be alone relied upon, litmus paper must be used towards the close of the operation in order to detect the precise point of saturation. Hence, after the liquid has become wine red, take care to add the sulphuric acid only by small portions, finally at the rate of only two drops at once, and after each addition of the acid draw the point of the stirring rod across a strip of blue litmus paper, one or two inches wide, so that red streaks may be formed upon the paper in regular order, and each streak correspond to a fresh addition of the acid. Proceed in this manner until the color of the liquid in the dish indicates that the point of saturation has been passed, then note the number of c. c. of acid which have been poured from the burette, dry the strip of litmus paper at a gentle heat, and observe which one of the streaks upon the paper just remains red when dry. The red color of all those streaks which were reddened with carbonic acid will com-

pletely disappear as the paper becomes dry, while the reddening due to sulphuric acid will remain visible; it is an easy matter, therefore, to determine how great an excess of the acid has been used, by simply counting the number of red streaks left upon the dry paper. A quarter of a cubic centimetre (or whatever two drops may amount to in terms of the burette employed) is then to be deducted from the total number of c. c. of acid used for every one of the streaks. Besides the sum of these drops used in excess, it is best to subtract also from the total amount of acid used one quarter of one c. c., which has gone to neutralize the alkali in the litmus employed for coloring.

Repeat the experiment with new portions of carbonate of sodium and of the acid, and in case the two results agree, proceed to dilute the acid to the desired degree in the manner already described.

For some eyes, an infusion of *Cochineal* possesses great advantages over the solution of litmus, as a means of recognizing the point of neutralization. To prepare the liquor, put 3 grammes of powdered cochineal in a flask, together with 50 c. c. of strong alcohol and 200 c. c. of distilled water, cork the flask and let the mixture digest for a day or two at the ordinary temperature, shaking it frequently. The clear solution, which may be either decanted or filtered from the residue, has a deep ruby-red color. On gradually diluting it with pure water, free from ammonia, it becomes orange, and finally yellowish-orange. Caustic alkalies and alkaline carbonates change the color to a carmine or violet carmine, and so do the alkaline earths and their carbonates; solutions of strong acids and acid salts make it orange or yellowish-orange, but to carbonic acid it is nearly indifferent. In using cochineal, the solution to be tested should not be heated. It is simply necessary to measure out a given volume, say 20 c. c. of the acid, to dilute it with about 150 c. c. of water, to add 10 drops of the cochineal liquor, and to pour in alkali from a burette until the yellowish liquor in the flask suddenly acquires a violet-carmine tinge through the action of a single drop of the alkali.

In nicer determinations it is important to bring the liquid each time to a given volume, by adding water after the neutralization is nearly finished. To note the level of the proper amount of liquid, say 200 c. c., strips of paper may be pasted upon the beakers or wide-necked flasks employed.

The same amount of coloring matter being thus always diffused in the same volume of the same water, errors due to varying degrees of dilution and varying amounts of ammonia, which is rarely absent from distilled water, are avoided. The contents of one flask, in which the neutralization has been satisfactorily effected, may be kept as a standard of color for the succeeding trials. The tint remains con-

stant for hours; it is unaffected by the carbonic acid of the air. When three or four concordant results have been obtained, the average is taken as expressing the relative strength of the acid and alkali. (Luckow, *Journ. prakt. Chem.*, **84**, 424, through *Amer. Journ. Sci.*, 1863, **35**, 280).

β. Mix concentrated sulphuric acid, of known specific gravity, with enough water that the mixture may contain rather more than one equivalent of the anhydrous acid for every 100 parts of liquid. Weigh out 1 to 1.5 grm. of pure anhydrous carbonate of sodium, place it in a flask or porcelain dish of 300 or 400 c. c. capacity, dissolve it in 100 or 150 c. c. of water, and pour into the liquid a measured quantity *a* of the cold acid. Take 1 c. c. of the acid for every 0.0053 grm. of the carbonate, so that the acid may be distinctly in excess. Boil the solution to expel the carbonic acid, then color it slightly red with a measured quantity of litmus solution and pour into the hot liquid, from a burette, a dilute solution of caustic soda of undetermined strength, until the last drop of the soda produces a distinct light blue color, unmixed with violet. If the solution is only slightly colored with litmus, and is free from carbonic acid, it is easy to determine the point of saturation with great exactitude, otherwise some difficulty is met with from the blue tint at first formed changing to violet.

Write down the number of c. c., *b*, of the soda solution required to neutralize the excess of acid. Then measure out a fresh portion, *c* ($= 20$ or 30 c. c.), of the dilute acid, and determine how many c. c., *b'*, of the soda solution are required to neutralize it. From this last determination it will appear that 1 c. c. of the soda solution is equivalent to $\frac{c}{b'}$ c. c. of the dilute acid. Hence there was employed in the previous experiment $\frac{b}{b'}c$ cubic centimetres more of this acid than would be needed to neutralize $a \times 0.0053$ grm. of carbonate of sodium; or $a - \frac{cb}{b'}$ cubic centimetres of the acid would have precisely neutralized the carbonate of sodium taken. Hence, if $a - \frac{cb}{b'}$ cubic centimetres of the acid be diluted with water to the bulk of *a* cubic centimetres, the solution will be normal. Compare Standard Nitric Acid, below.

Standard sulphuric acid may be prepared also by decomposing a known weight of sulphate of copper with sulphydric acid, as proposed by Gibbs (*Amer. Journ. Sci.*, 1867, **44**, 210). Put a quantity of pure powdered sulphate of copper in a porcelain crucible placed within a Hessian crucible, and heat the sulphate for about an hour, taking care to raise the temperature gradually, and that the heat shall at no time exceed low redness. Transfer the hot anhydrous sulphate to a dry weighing tube, close the tube, and after it has become

cold weigh out a quantity of the sulphate. Dissolve the weighed sulphate in water, heat the solution to boiling, pass a stream of sulphuretted hydrogen through it to precipitate the copper (see Acidimetry), and dilute the filtrate and wash water to a known volume. The quantity of sulphuric acid in the solution is known from the weight of the anhydrous sulphate taken.

For technical determinations it is convenient to make the standard acid of such strength that 50 c. c. of it will exactly neutralize 5 grms. of pure carbonate of sodium. Such acid may be used for testing the value of either of the caustic or carbonated alkalies; and the number of half c. c. of it required to produce saturation, in any particular case, will correspond directly to the per cent of alkaline carbonate or caustic alkali contained in the sample tested, provided there be weighed out for the analysis a quantity of material equivalent to 5 grms. of carbonate of sodium. The equivalent quantities capable of saturating 50 c. c. of this standard acid are respectively:—

For Carbonate of Sodium	5.000 grms.
" Hydrate " " " " " " "	5.619 "
" Carbonate of Potassium	6.519 "
" Hydrate " " " " " " "	5.292 "

If 5 grms. of an impure carbonate of sodium, or 6.519 grms. of common pearlash be weighed out and titrated with the acid in question, the number of half c. c. used will in the one case give the per cent of pure carbonate of sodium, and in the other of pure carbonate of potassium, which the samples contain, without need of any calculation. Where substances poor in alkali are to be tested, some multiple of the numbers above given may be weighed out.

Standard Chlorhydric Acid. Mix 900 c. c. of water with 180 c. c. of chlorhydric acid of 1.12 specific gravity, measure out with a burette two portions of from 10 to 20 c. c., and determine the quantity of chlorhydric acid in each portion by precipitation, as Chloride of Silver. If the two results are concordant, take the mean and calculate therefrom how much water must be added to the acid tested to reduce it to the normal strength. If it were found, for example, that 20 c. c. of the acid contained 0.81 grm. of HCl, then a litre would contain 40.5 grms. and

$$\text{Mol. wt. of HCl} = 36.5 : 1000 :: 40.5 : x \quad (x = 111).$$

so that 111 c. c. of water would have to be added to each litre of the acid.

Instead of determining the amount of chlorhydric acid by precipitation, as chloride of silver, it may be estimated with carbonate of sodium in the manner described above, under standard sulphuric acid; but before boiling the liquid to expel carbonic acid, a few grammes of sulphate of sodium must be added to prevent the evolution of chlorhydric acid. Or it may be estimated with carbonate of calcium,

as will be described directly under Standard Nitric Acid.

Standard Oxalic Acid. Weigh out 63 grms. (the weight of one equiv.) of crystallized oxalic acid, transfer it to a litre flask, add water enough to nearly fill the flask, shake the mixture until the acid has all dissolved, bring the liquid to the temperature of 16°, and pour in water up to the litre mark; again shake the solution thoroughly, then pour it into a stoppered bottle and keep it protected from sunlight. Since the oxalic acid found in commerce is usually contaminated with potassium, it is best to prepare a pure acid directly by acting upon starch with nitric acid, and recrystallizing the product. (See Oxalic Acid).

Standard Nitric Acid may be readily prepared by the method described above in § 3, under the head of standard sulphuric acid. Instead of carbonate of sodium, carbonate of calcium may be employed. It has the advantage of being more readily obtained in a state of purity than carbonate of sodium. An outline of the process may here be re-stated:—Prepare a quantity of dilute nitric acid, in such wise that the strength of this acid, as indicated by the hydrometer, shall be somewhat greater than that of the desired standard acid. Prepare also a solution of caustic soda, about as strong as the acid, and determine by titration how many c. c. of this soda solution are required to neutralize a measured quantity of the acid. Weigh out about 1 grm. of pure carbonate of calcium (either powdered Iceland spar or the precipitated carbonate) which has been dried at 100°, and dissolve it in a measured quantity of the nitric acid. Heat the mixture gently to expel carbonic acid, color it with litmus, and finally pour into the liquid as much of the soda as is needed to neutralize the nitric acid which was used in excess. Note the quantity of soda solution employed, calculate therefrom the number of c. c. of nitric acid which were used in excess, and subtract this amount from the total amount of acid taken to dissolve the carbonate. The remainder will give the number of c. c. of acid which are equivalent to the weighed quantity of carbonate of calcium; in other words, it will indicate what portion of the acid was neutralized by the calcium salt. The weight of dry acid in this portion may now be found by the proportion:

$$\begin{array}{l} \text{Equiv.} \\ \text{CaCO}_3 \end{array} : \begin{array}{l} \text{Wt. of} \\ \text{taken} \end{array} = \begin{array}{l} \text{Equiv.} \\ \text{N}_2\text{O}_5 \end{array} : \begin{array}{l} \text{Wt. of} \\ \text{taken} \end{array} = \begin{array}{l} \text{Wt. of} \\ \text{CaCO}_3 \end{array} : \begin{array}{l} \text{Wt. of N}_2\text{O}_5 \text{ in the volume} \\ \text{of liquid neutralized} \\ \text{by that CaCO}_3. \end{array}$$

The value of the acid having thus been determined, proceed to dilute what remains of it to the required standard, in the manner already described. (Standard Sulphuric Acid).

In some cases it may be found convenient to employ a standard solution of carbonate of sodium instead of the dry salt. The standard solution may be prepared with ease by simply dissolving a weighed quantity of pure car-

bonate of sodium in the required volume of water. By using measured portions of this solution the operator has it in his power to make several titrations from the product of a single weighing. Reischauer (*Dingler's polytech. Journ.*, 187. 47) recommends the use of a normal solution of the carbonate, made by dissolving 53 grms. of the salt to the volume of a litre. To prepare a standard acid by means of this solution, measure off 10 c. c. (= 0.53 gm.) of it with a pipette, mix it with an excess of the acid to be standardized, and neutralize this excess with caustic soda, as above described.

Merits of the several Acids. Test acid may be prepared more simply and directly from oxalic acid than from either of the other common acids. Oxalic acid may readily be made pure and dry, in spite of current assertions to the contrary, and were it not for a certain tendency to decomposition which is exhibited by aqueous solutions of this acid when exposed to light, they would doubtless be very generally employed in processes of alkalimetry.

Chlorhydric acid has special merit, in that the fundamental determination of the proportion of acid in any given sample may be made with very great accuracy by precipitation, as chloride of silver.

Sulphuric acid, which is perhaps more frequently employed than either oxalic or chlorhydric acid, has the advantage of being less volatile than the latter, and less liable to change than the former. Dilute solutions of sulphuric acid may be boiled freely without fear of loss. When standard chlorhydric acid, on the contrary, has to be boiled, it is best to mix with it a quantity of sulphate of sodium to hinder the evolution of chlorhydric acid. In any event, care should be taken both with chlorhydric and nitric acids, that only a very slight excess of acid be present when a liquid is to be boiled. Nitric acid has no advantage over chlorhydric acid, excepting that it volatilizes somewhat less readily than the latter when a dilute solution is boiled.

Sulphuric acid is well suited for the estimation of sodium, potassium and magnesium, but cannot be used for determining calcium, barium or strontium; either nitric or chlorhydric acid must be employed when the oxides, hydrates or carbonates of these metals are to be titrated.

Tartaric acid, at one time proposed as a substitute for sulphuric acid in alkalimetry, is not well adapted for use as a standard acid, since aqueous solutions of it are liable to decompose on standing.

The Actual Determination of the proportion of alkali in any sample of unknown value, follows, from what has been said above, without need of further description. A weighed quantity of the material to be tested is dissolved in about 200 c. c. of water, the solution is colored with 1 or 2 c. c. of litmus, and standard acid is

poured upon it from a burette until the alkali is saturated. (See standard sulphuric acid α). Or an excess of the standard acid is added in the beginning to the weighed sample of alkali, the mixture boiled to expel carbonic acid, and the excess of the standard acid estimated with a standard solution of caustic soda. (See Acidimetry and standard sulphuric acid β).

The quantity of material to be taken for analysis in any particular case, may be judged of, from what has been said above, under standard sulphuric acid. In order to diminish the errors incidental to weighing, it is often best, in the lack of a delicate balance, to weigh out a quantity of material ten times as large as is really wanted. The weighed substance is then dissolved in half a litre of water, and one or two portions of it, each of 50 c. c., are taken out with a pipette for analysis. In case any portion of the weighed substance refuses to dissolve in water, the liquid should be filtered and the residue washed before proceeding to the acid treatment, or better, the liquid may be allowed to stand until it has become clear, and a definite portion of the clear liquor then taken up with a pipette for the analysis. Care must of course be taken, in the first place, to obtain a fair sample of the material to be tested by taking small portions of it from many parts of the entire mass and rubbing them thoroughly together in a mortar.

According to Baugart & Wildenstein (*Zeitsch. analyt. Chem.*, 1864, 3. 324), it is well, in technical determinations of the value of alkaline carbonates, to check the frothing, which occurs when acid is added to the liquor, by means of a layer of melted paraffine. A small quantity of paraffine thrown upon the boiling solution of carbonate of sodium, contained, as usual, in a large evaporating dish, will immediately melt and spread over the entire surface of the liquor, in such manner that no permanent froth can form upon the surface of the liquid. The titration may consequently be proceeded with without delay or interruption. A few decigrammes of paraffine are sufficient for a surface 12 c. m. in diameter. In order to reduce the paraffine to convenient shape, dip a not too thin glass rod into a quantity of melted paraffine, bring the rod close to the surface of a quantity of cold water, and then allow the drops of the hot liquid to fall into the water. Dry the solidified drops on filter paper and keep for use; 2 or 3 of them will be found sufficient for a single alkali determination.

Estimation of the proportion of Caustic Alkali and of Alkaline Carbonate in mixtures containing both these substances.

Weigh out from 15 to 20 grms. of the impure carbonate to be tested, and dissolve it in water in a quarter-litre flask. When the soluble portion of the substance has all dissolved, fill the flask with water to the mark and shake its contents thoroughly. Cork the flask in

order to exclude the carbonic acid of the air, and allow the liquid to stand until it has become clear. Draw off with a pipette two portions of the solution, each of 100 c. c., and determine the total amount of alkali in one portion by titration with a standard acid. This "total alkali" may be set down either as carbonate of the alkali, or as caustic alkali, according as one or the other of these ingredients preponderates in the sample under examination. Allow the other 100 c. c. portion of the solution to flow into a quarter-litre flask, add to it 100 c. c. of water and a solution of chloride of barium, as long as a precipitate falls. Fill the flask with water to the mark, cork it and leave the mixture at rest, until all the carbonate of barium has been deposited and the liquid has become clear. Draw off 100 c. c. of the clear solution, color it with litmus, add standard chlorhydric acid to distinct acid reaction, and note the quantity of acid used. Neutralize the excess of acid with a standard solution of caustic soda, and subtract this excess from the whole amount of acid taken. The difference will give the amount of acid which has been neutralized by the caustic alkali in the portion of material subjected to analysis, and from the weight of the acid, that of the alkali equivalent to it may readily be found by calculation. Finally subtract the weight of caustic alkali thus obtained from the total weight of alkali as found by titration in the other portion of the solution, in order to obtain the amount of alkali which must be regarded as a carbonate.

According to A. Mueller, the solution to which chloride of barium has been added must not be filtered. It contains caustic baryta as well as caustic alkali and alkaline chloride. It is found that a filter retains some of the baryta, and that a little of the caustic alkali might thus be lost.

Another method of estimating caustic alkali when mixed with an alkaline carbonate, will be given below, under Principle II.

Principle II. Volatility of carbonic acid.

Applications. Determination of the amount of pure alkaline carbonate in saleratus and the other commercial carbonates of sodium and potassium.

Method. A weighed quantity of the alkaline carbonate to be examined is treated with an excess of sulphuric acid in an appropriate apparatus (see Carbonic Acid), and the weight of the carbonic acid expelled from it is determined either by weighing the apparatus before and after the experiment, and calling the loss carbonic acid, or by absorbing the gas in soda lime and weighing it as such. (See Carbonic Acid). From the quantity of carbonic acid found, the proportion of alkaline carbonate in the sample tested is obtained by calculation:—

$$\begin{array}{ccccccc} \text{Equiv.} & \text{Equiv. wt.} & \text{Weight} & \text{Wt. of Na}_2\text{CO}_3 & & & \\ \text{wt. of :} & \text{of Na}_2\text{CO}_3 & \text{of CO}_2 & \text{or of K}_2\text{CO}_3 & \text{:} & \text{=} & \\ \text{CO}_2 & \text{(or of K}_2\text{CO}_3) & \text{found} & \text{in the sample,} & & & \end{array}$$

The process yields tolerably good results, but is less accurate and far less convenient and expeditious than the method by neutralization with a standard acid. It is consequently seldom employed in practice. It was at one time somewhat used for determining the proportion of alkaline carbonate in mixtures of caustic and carbonated alkali, after the total alkali value of the sample had been ascertained. The best way of determining the total alkali value is by titration with a standard acid, either directly or indirectly, as has been already described. But in lack of an acid of determined strength, the total alkali value of any sample of mixed caustic and carbonated alkali may readily be determined by the method of expelling carbonic acid. To this end expose a portion of the sample to carbonic acid gas, until all the caustic alkali present has been saturated, ignite to destroy any bicarbonate which may have been formed, and finally determine the carbonic acid in the manner already described. In another portion of the original sample, which has been subjected to no treatment, except drying, determine the amount of alkaline carbonate. The difference between the two determinations will indicate the proportion of caustic alkali in the substance analyzed.

Another method of estimating caustic alkali in presence of an alkaline carbonate, will be found above, under Principle I.

Each of the processes of alkalimetry above described is liable to error when the substance to be tested is contaminated with certain impurities. The special precautions to be taken in order to correct or avoid these errors, will be described further on, under the heads of the several alkalies and alkaline carbonates. For the methods of estimating potassium in presence of sodium, see KCl; 2KCl, PtCl₄; KClO₄; K₂SO₄.

Aluminate of Ethylamin. See Aluminate of Sodium.

Aluminate of Potassium. See Aluminate of Sodium.

Aluminate of Sodium.

Principle. Solubility in water.

Applications. Separation of Al from Fe, and from small quantities of Mn. Also from Co and Ni (Method B). Method B is specially adapted for the treatment of mixtures of the oxides of iron and aluminum which have been ignited, and so rendered insoluble in caustic lyes.

Method A. Evaporate the chlorhydric acid solution of aluminum, etc., to dryness on a water bath, in order to remove the excess of acid. Take up the residue with water, and in case the solution is cloudy, add a drop of strong chlorhydric acid and warm the mixture upon the water bath to clear it. Pour slowly a quantity of not too dilute soda or potash lye into a porcelain dish, or better, into a large platinum or silver crucible; place the dish or

crucible upon a water bath and heat the latter to boiling. Stir the hot lye with a stiff platinum wire, and slowly pour into it the solution of aluminum, etc. Each particle of the aluminum compound is thus brought into intimate contact with a large excess of free alkali, and is converted into a soluble aluminate of the alkali, while the iron is thrown down as a hydrate. When the last portion of the aluminum solution has been washed into the dish which contains the alkali, pour the alkaline mixture upon a filter, wash the ferric hydrate and precipitate the aluminum from the filtrate, as Hydrate of Aluminum, by boiling the liquor with an excess of chloride of ammonium. (Læwe, *Zeitsch. analyt. Chem.*, 1865, 4, 357).

After a little experience, the amount of alkali to be employed may be judged of from the quantity of residue left on evaporating the chlorhydric acid solution of aluminum, etc. In most cases, two or three grms. of solid hydrate of sodium will be enough for a single operation. If the mixture to be analyzed contains a large proportion of iron, the ferric hydrate precipitated by the alkali will retain a certain amount of alumina. It is best, therefore, when the amount of ferric hydrate is large, to redissolve the washed precipitate in chlorhydric acid, to evaporate the chlorhydric acid solution as before, and to pour the neutral or nearly neutral solution into a new quantity of hot soda lye. This second alkaline solution must of course be added to the first, after filtering to separate the ferric hydrate, before proceeding to precipitate the aluminum. After the ferric hydrate has been thoroughly washed with hot water to remove the aluminate of sodium, it must be again washed with a hot, but not too strong, solution of chloride of ammonium, to remove a small quantity of alkali which would otherwise be retained by the precipitate. The precipitate is finally washed with hot water until the filtrate no longer gives any reaction when tested with nitrate of silver. Since the aluminum is to be thrown down with chloride of ammonium, the saline wash liquor, above mentioned, need not be kept separate from the remainder of the filtrate.

An older method of procedure is to add the alkali to the solution of aluminum and iron, instead of pouring the aluminum solution into the alkali. In any event, the iron and aluminum are usually precipitated together as hydrates in the first place, and the mixed precipitate collected on a filter and washed. In the old process the subsequent operations are as follows:—Scrape the moist precipitate from the filter with a platinum spatula, and place it in a porcelain, or better, a platinum dish. Set the dish beneath the funnel which holds the filter, and pour drops of hot chlorhydric acid into the latter until all the precipitate which had adhered to it has dissolved. Remove the dish and concentrate its contents, if need be;

wash the filter with warm water and collect the washings in a beaker. Add concentrated soda lye to the liquid in the dish until the excess of acid is almost neutralized. Heat the liquid to boiling, remove the lamp and place in the dish a lump of hydrate of sodium or hydrate of potassium, large enough to dissolve all the aluminum which the mixture contains. If the proportion of iron in the mixture be small, the precipitate produced by the soda will, after a short time, contain little or no aluminum, but only ferric or manganic hydrate. Pour the contents of the dish into the beaker which contains the rinsings of the filter, and wash the dish thoroughly with water. Filter off the aluminate of sodium from the insoluble precipitate, wash the latter with boiling water, dissolve it in chlorhydric acid, and precipitate the iron as Hydrate of Iron. Acidulate the filtrate with chlorhydric acid, and precipitate the aluminum as Hydrate of Aluminum.

Since the residual ferric hydrate is liable to retain 1 or 2 per cent of hydrate of aluminum, it must be redissolved in chlorhydric acid, and the solution treated with caustic soda, as before, to ensure the complete removal of the aluminum, unless, indeed, the ferric precipitate is so small that the actual weight of the aluminum contained in it is insignificant.

In the foregoing cases the iron is supposed to be in the form of a ferric salt, but some chemists prefer to reduce the iron to the condition of a ferrous salt, by means of a solution of sulphurous acid, or of sulphite of sodium, before proceeding to separate it from aluminum. Their method is as follows:—Heat the tolerably concentrated, acid solution of aluminum, etc., to boiling, in a flask or capacious dish, best of silver or platinum, remove the lamp and add enough sulphite of sodium to reduce the iron completely to the state of protoxide. Again heat the liquor to boiling, keep it boiling for some time, and neutralize the acid with carbonate of sodium, added cautiously by small pieces. Pour in an excess of caustic soda or potash lye (or of ethylamin), and continue to boil sometime longer. If much iron be present, the voluminous white precipitate of ferrous hydrate thrown down at first will finally be converted into black, granular ferroso-ferric oxide. Remove the lamp and allow the mixture to settle; pour the clear liquid into a filter made of not too porous paper; boil the precipitate with a fresh quantity of soda lye, and wash it thoroughly with hot water, first by decantation, and afterwards upon the filter. The aluminum is determined in the filtrate as Hydrate of Aluminum.

Precautions. If, as is often the case, the mixture of aluminum, etc., to be analyzed, contains magnesium, a portion of the latter will be left combined with the ferric hydrate upon the filter. Some aluminum is also likely to remain undissolved in combination with the

magnesium. So, too, in presence of calcium some aluminum is apt to escape solution. If chromium be present, most of it will remain undissolved with the hydrate of iron, but a small quantity sometimes oxidizes and passes into the filtrate as chromate of sodium.

In case the iron is reduced by sulphite of sodium, the liquid is liable to bump violently before it actually boils. To prevent this bumping a spiral coil of platinum wire may be placed in the liquid, or the flask may be shaken continually until its contents boil. When boiling has once begun the bumping ceases.

Special care must be taken that the soda or potash used be free from aluminum and silicon. The use of a porcelain dish should be avoided if possible, since portions of the dish are dissolved by the hot alkali, and impurities thereby added to the substance to be analyzed.

Method B. Fuse the mixed oxides of aluminum, iron, cobalt and nickel, with hydrate of sodium or of potassium, in a silver crucible. Boil the cold mass with water and filter to separate the soluble aluminate from the other oxides, which remain undissolved. The residual oxides, though free from aluminum, hold a certain proportion of sodium or potassium in combination, as well as a small quantity of oxide of silver derived from the crucible. The silver remains as an insoluble powder (chloride of silver) when the ferric oxide is treated with chlorhydric acid.

Anhydrous oxide of aluminum, as it occurs in nature, is not readily attacked by alkalis. Chenevix, for example (cited in *Pfaff's Handbuch analyt. Chem.*, 1824, 1. 449), found that the mineral corundum could not be decomposed by intense ignition with 6 times its weight of caustic potash. To effect solution the mineral should be fused with bisulphate of sodium. Chenevix fused with 200 to 250 parts of borax glass, and treated the product with chlorhydric acid.

Aluminum

Is weighed in the form of anhydrous sesquioxide. It is usually precipitated as a hydrate, though sometimes as a basic acetate or formate, or as oxide. For the separation of aluminum from the other metals, see the reference list in the Appendix.

Ammonia.

(Compare Nitrogen, Nitrogen compounds, and Hydrate of Ammonium).

Principle I. Comparative lightness of the aqueous solution, in proportion as it contains more ammonia.

Application. Technical estimation of the value of ammonia-water.

Method. Take the Specific Gravity of the liquor with a Hydrometer, and refer to the tables of "specific gravity and per cent ammonia," in any dictionary of chemistry. Compare Acidimetry (Method by specific gravity). The liquid tested must contain no other soluble

substance besides water and ammonia. In case the matter under examination be contaminated with any non-volatile impurity, distil off a large fraction of a measured portion of the liquid, as described under Alcohol (volatility or), and take the specific gravity of the distillate. If any portion of the ammonia is combined with an acid, mix a quantity of alkali with the liquid before distilling it, as explained below under the principle Volatility. (*Pfaff, Handbuch analyt. Chem.*, 1825, 2. 25). The process is far inferior to those which depend upon the neutralization of ammonia by standard acids.

Principle II. Power of neutralizing acids.

Applications. Estimation of ammonia in its aqueous solution. Absorption of ammonia gas by acids. Use of ammonia-water as a neutralizer and precipitant, in a multitude of cases, and as a standard alkali in Acidimetry.

Method A. To estimate ammonia in a solution, weigh or measure out a quantity, say 10 c. c. of the sample to be tested, add 1 or 2 c. c. of litmus solution, and saturate with a standard acid in the manner described under Alkalimetry. Or measure out a definite quantity of the standard acid, color it with litmus, and saturate with the ammonia to be tested. In either case, the point of saturation is hit without difficulty. It is well always to weigh a definite volume of the liquid to be tested, for by dividing the weight of the liquid in grms. by its volume in c. c., we obtain the specific gravity of the solution, and may subsequently dispense with the balance in case any new portion of the liquid has to be taken for analysis. The method of supersaturating the ammonia-water with standard acid and determining the excess of acid with a standard soda solution, is not to be recommended, since ammonium salts, even when neutral, color litmus violet.

Method B. Slightly supersaturate the ammonia with chlorhydric acid, evaporate to dryness at 100° to 200°, and weigh the chloride of ammonium. Or (after Mohr, *Titrimethode*, 1855, 2. 58) estimate the chlorine in the dry chloride of ammonium with a dilute standard solution of nitrate of silver (see Chloride of Silver), and calculate how much ammonium would be equivalent to this chlorine.

With regard to the use of ammonia as a reagent, the analyst should remember that the ordinary ammonia-water of commerce is often impure. Besides more or less carbonate of ammonium, it is liable to contain no inconsiderable quantity of a soluble compound of iron and organic matter, which is apt to be dragged down by gelatinous precipitates, and to interfere in many ways with the accuracy of analyses.

For quantitative work, chemically pure ammonia-water should either be procured from a manufacturer of fine chemicals, or prepared

expressly by distilling from a glass flask a mixture of 1 part of pure chloride of ammonium, 1.25 parts of slaked lime, and 1 to 1.25 parts of water. The distillate is received in three Woulfe bottles; of which the first, charged with a small quantity of water, or milk of lime, serves to wash the gas. The second bottle should contain about as much water, by weight, as there is chloride of ammonium in the flask, or in case a saturated solution is required, take two-thirds of this weight of water; the bottle should not be more than three-quarters full at first, to allow for expansion. The third bottle should contain but little water. All the bottles should be set in a dish of cold water to facilitate the solution of the gas. Heat the flask upon a sand bath, taking care to avoid foaming, until half the water has distilled from it.

Ammonia-water should be kept in glass-stoppered bottles. It should leave absolutely no residue when evaporated to dryness, should give no precipitate when diluted and tested with lime-water, or with chloride of barium; or when tested with sulphuretted hydrogen or nitrate of silver, after acidulation.

Principle III. Volatility.

Applications. Separation of ammonium from all the elements. Estimation of ammonia in rain and river water (Method A). Estimation of ammonia in copulate ammonio-compounds, in urine, manures, etc. (Methods B and C).

Method A. The mixture is boiled with caustic soda, potash, lime, or baryta.

1. Prepare a distillatory apparatus as follows: Fit to a glass flask a perforated cork or caoutchouc stopper carrying a short delivery tube bent at an obtuse angle; by means of a rubber connector attach this delivery tube to the head of a small worm or of a short Liebig's condenser, the lower end of which passes through a perforated cork into a capacious tubulated receiver; and to the second orifice of the receiver attach a U tube, by means of bent glass connections. According to S. W. Johnson, the worm or condensing tube should be made of block tin, since glass yields a sensible amount of alkali to hot steam.

Pour into the flask as much of a moderately strong solution of caustic soda, caustic potash, or milk of lime, as will fill something more than a third of it. Place the flask in a slanting position upon a wire gauze support and boil its contents until every trace of ammonia, with which the alkali may have been contaminated, is removed. Then cork the flask and leave it until its contents have become thoroughly cold.

Weigh out the substance to be analyzed in a glass tube, 3 or 4 c. m. long by 1 c. m. wide, closed at one end. Place the tube and its contents in the flask after the latter has become cold, and connect the flask with the condensing apparatus.

Measure off a quantity of standard oxalic,

chlorhydric or sulphuric acid (see Acidimetry), more than sufficient to absorb all the ammonia which can possibly be expelled from the substance taken, and mix it with 2 or 3 c. c. of a solution of litmus. Pour a little of this acid into the U tube of the apparatus, but no more than will fill the lower part of the tube in such manner that bubbles of air can readily pass through the liquid. Pour the rest of the measured quantity of acid into the tubulated receiver, together with a little water.

After proving that all the joints of the apparatus are tight, heat the flask until its contents boil slowly, and continue the operation until some time after the drops of water falling from the condenser have ceased to give the least tinge of blue at the moment when they strike the liquid in the receiver.

Pour the contents of the receiver and U tube into a beaker, rinse with water and determine the amount of free acid in the liquid by titration with a standard solution of caustic soda (see Acidimetry). By subtracting the amount of acid thus found from the quantity of acid originally taken, we obtain the amount of acid which has been neutralized by the ammonia. The amount of the latter is then calculated (see Alkalimetry).

This method affords accurate results, and can be used in all cases where the substance to be analyzed contains no nitrogenized matter, other than ammonium salts, capable of decomposition by caustic lyes. It is to be observed that the flask in which the decomposition is effected must be placed in a slanting position, so that no particles of the fixed alkaline liquid can be thrown into the delivery tube by the movement of ebullition, and that the end of the condenser must not dip into the liquid in the receiver.

If it be desirable to weigh the ammonium in the form of a solid rather than to estimate it by titration, the receiver and U tube may be charged with chlorhydric acid, and the ammonium weighed as Chloride of Ammonium or as Chloroplatinate of Ammonium.

2. Place a litre of the water to be examined in a retort capable of holding at least four litres, add to the liquid 25 c. c. of baryta water,—or in place of the baryta, lime, potash or soda,—to retain the carbonic acid. Connect the retort with a condensing apparatus, and distil the water slowly until the distillate amounts to a quarter litre. Determine the proportion of ammonia by titrating with normal sulphuric acid (Boussingault), or determine the ammonia in the distillate by Nessler's test. See Iodide of Mercurammonium (Miller).

3. For determining ammonia in urine, F. Mohr (*Titrirmethode*, 2. 216) has proposed, in place of Method C, the following modification of the process:—Carefully neutralize the urine with a dilute solution of caustic potash, add to the neutral liquor a measured quantity of standard potash, more than sufficient to decom-

pose all the ammonium salts in the solution, boil the mixture as long as ammonia continues to be evolved, and finally, without heeding the ammonia which is set free, determine the amount of caustic alkali left in the urine, by means of a standard acid.* The points of neutralization are determined in both cases by means of litmus paper. The presence of urea does not affect the accuracy of the results, although this substance is decomposed by boiling potash, nor does hippuric acid do any harm. In cases where no great degree of accuracy is demanded, the process appears to be applicable for testing human urine, though in that case it indicates rather less ammonia than the processes of Schloesing and Boussingault. But for testing the urine of cattle it cannot be relied on. Rautenberg (*Zeitsch. analyt. Chem.*, 1863, 4, 500) has shown that with the urine of oxen Mohr's method always indicates a larger proportion of ammonia than can be obtained by the methods of Schloesing and Boussingault, the accuracy of both of which has been well established. This apparent excess seems to be due to the decomposition of various ingredients of the urine which, though originally neutral, become acid when exposed to the action of boiling potash, and so neutralize a portion of the standard alkali.

Method B. The Ammonium Compound is heated in a combustion tube with an excess of Soda-Lime, in the manner described under Nitrogen. The ammonia is collected in acid and determined as in Method A.

Method C. The Ammonia is set free by Hydrate of Calcium, or by potash or soda lye, at a low temperature.

1. *By ebullition in vacuo* (Boussingault's process, *Mémoires de Chimie Agricole*, Paris, 1854, p. 292). To a strong flask of about 1 litre capacity, fit tightly a cork carrying one straight tube provided with a stop-cock and one gas delivery tube, bent at a right angle. The straight tube should reach to within a few m. m. of the bottom of the flask, while the bent tube merely passes through the cork. By means of a short piece of rubber tubing tied tightly to the glass, connect the gas delivery tube with another glass tube of similar bore, bent at a right angle and reaching nearly to the bottom of a narrow cylinder proper to receive a charge of standard acid. The cylinder is fitted with a cork, and is connected by means of a second bent glass tube, provided with a stop-cock, with the receiver of an air pump. The corks of the apparatus must fit tightly enough to support the external pressure which will be exerted upon them by the atmosphere, when the air is pumped out from within the vessels. To strengthen the corks it is well to wind about their heads strips of sheet cork or of sheet lead, so that the head thus thickened may be as wide as the neck of the flask. The whole may then be bound firmly together by means of strips of sheet caoutchouc, wide

enough to reach from the top of the cork to a point an inch or more below the rim of the flask. The caoutchouc is finally tied firmly with twine, both to the neck of the flask and to the head of the cork. When everything is ready, place 10 c. c. of standard acid in the cylinder (Boussingault uses sulphuric acid strong enough that 10 c. c. shall saturate 0.2125 grm. of ammonia), and set the cylinder in a beaker of cold water—ice water is best, though the apparatus gives satisfactory results when the temperature of the water is as high as 12° or 15°. Pour into the flask 50 grms. of the urine to be tested, add to it about 5 grms. of slaked lime, cork the flask and set it in a water bath so arranged that it may be kept constantly at a temperature of 35° to 40°. Close both the stop-cocks upon the apparatus, exhaust the receiver of the air pump, and then slowly open the stop-cock on the tube which connects the receiver with the cylinder charged with acid. The liquid in the flask will soon begin to boil. When this happens, close the cock again, and leave the apparatus to itself. Since the cylinder which contains the acid is comparatively cold, the vapors distilled from the flask immediately condense in it. The liquid in the flask consequently continues to boil tranquilly, and after a short time will evaporate completely, so that nothing but a dry residue is left in the flask. In order to sweep forward any ammonia vapor which may be left in the flask, open the stop-cock above it slowly, so that air may enter. Then close the stop-cock, exhaust the receiver, and slowly open the second stop-cock beyond the acid cylinder, so that the air in the flask may be drawn forward through the acid. Finally determine with a standard alkali (Boussingault uses a solution of lime in sugar water) how much of the standard acid originally taken is still left unsaturated in the absorption cylinder. (See Acidimetry). The process requires far less time than No. 2, and is equally accurate. It has the disadvantage of requiring comparatively complex apparatus.

Instead of this method of ebullition in vacuo, Boussingault has attempted to remove the ammonia from mixtures of urine and slaked lime by means of a current of air made to bubble through the liquid continually through 4 or 5 hours, at the temperature of 35° or 40°; but without good results, for a part of the ammonia was always retained in the solution. To ensure the complete and speedy evolution of the ammonia in this way, Boussingault found that the solution must be heated to 90° or 100°. But these high temperatures are inadmissible in the analysis of urine, for ammonia would be formed through the decomposition of the urea which the urine contains.

2. *By Exhalation at the Ordinary Temperature.* (Schloesing's method). Select a shallow, flat-bottomed capsule 10 or 12 c. m. in diameter and weigh it. Measure out something less

than 35 c. c. of the liquid to be tested, and place it in the dish. Weigh the dish and liquid. Then set the dish on a common dinner plate filled with mercury. Bend a thick glass rod into the form of a tripod, place this tripod in the capsule which contains the solution to be tested, set upon it another shallow dish which has been charged with 10 c. c. of standard oxalic or sulphuric acid (see Alkalimetry), and invert a beaker over the whole. Fill a pipette, provided with a wide aperture, with milk of lime, lift up one side of the beaker as far as may be necessary, and allow the contents of the pipette to flow into the solution of the ammonium salt. Immediately replace the beaker and put a weight upon it, so that its lower edge shall be pressed into the mercury. After 48 hours lift the glass at one side and thrust a bit of moistened red litmus paper into the atmosphere within; if the color of the paper remains unchanged, the first stage of the operation is finished; but if the paper become blue the glass must be replaced, and the apparatus left to itself for another term of hours. When all the ammonia has been expelled from the original solution, and has been absorbed by the standard acid, determine how much free acid is left, by titration with a standard solution of caustic soda (see Acidimetry), and calculate the amount of ammonia from that of the acid which it has neutralized.

Instead of the beaker and plate of mercury above described, a bell glass with ground rim may be placed air tight upon a greased ground glass plate. A tubulated bell provided with a ground glass stopper is to be preferred, since, in this case a strip of litmus paper attached to a thread may be introduced into any part of the jar without lifting the latter.

Method C, in both its modifications, is useful in cases where the presence of organic matters decomposable by boiling alkalis precludes the use of Method A. — Reischauer (*Zeitsch. analyt. Chem.*, 1864, **3**, 138) has shown that even after six months' action, cold potash or soda lye has no power to set free ammonia from cyanogen compounds.

According to Schloesing, 48 hours are always sufficient to expel 0.1 to 1 gramme of ammonia from 25 to 35 c. c. of solution; but Fresenius has found that this statement is true only with regard to quantities less than 0.3 gm. When the quantity of ammonia exceeds 0.3 gm., 48 hours is often insufficient for the complete expulsion of the ammonia; it is well, therefore, to operate, if possible, upon quantities of substance which contain no more than this proportion.

Ammonium.

For the separation of ammonium from the several elements, see finding list in Appendix.

Ammonium is usually determined as chloride, chloroplatinate or tartrate; or by titrating ammonia-water with an acid of determined

strength. Sometimes the nitrogen of an ammonium compound is collected and measured, and the amount of ammonium calculated from that of the gas. Ammonium may be separated from all metals excepting those of the alkalis by precipitating the metals by means either of H_2S , $(\text{NH}_4)\text{HS}$, $(\text{NH}_4)_2\text{CO}_3$, or Na_2HPO_4 .

Ammonium Salts.

(Compare Nitrogen and Nitrogen Compounds.)

Principle. Volatility.

Applications. Separation of certain ammonium salts from salts of Li, Na, K; Ba, Ca, Sr; Mg, Zn, Cd; Al, Cr, Ur, Mn, Fe, Co, Ni. The ammonium salt must be wholly volatile, and the mixture to be examined free from other volatile or decomposable matters.

Methods.

1. *Separation of Ammonium Salts from Salts of Na, Li, K; Ba, Sr, Ca, Mg and Cr.* In case the dry mixture to be examined contains but a single acid, such as chlorhydric or sulphuric acid, heat a weighed portion of it to faint redness in a covered platinum crucible, as long as any fumes are evolved. The difference between the weight of the crucible and contents before and after the ignition gives the weight of the ammonium salt. The crucible must be heated gently at first, but must afterwards be kept for some time at a dull red heat. In case the salts are sulphates, the crucible must be heated with special care, in order to avoid loss of material through decrepitation of the sulphate of ammonium, and the residue must finally be ignited in an atmosphere of carbonate of ammonium (see Sulphate of Potassium) for the purpose of decomposing a quantity of acid sulphate of potassium, which is formed by the decomposition of a part of the sulphate of ammonium. — If the mixture to be analyzed contains more than one acid, it may be moistened with a quantity of free acid, similar to the least volatile of the acids in the mixture, and evaporated to dryness upon a water bath. The operation should be repeated several times, or until the more volatile acids have been completely expelled. A mixture of chloride of ammonium and sulphates of the alkali metals cannot be analyzed in this way, for on igniting the mixture the sulphates would be wholly, or in part, converted into chlorides.

2. *Separation of Ammonium Salts from Salts of Zn, Cd, Al, Ur, Mn, Fe, Co, Ni.*

If there is no chloride of ammonium in the mixture to be analyzed, a weighed quantity of the mixture may be ignited directly, as in No. 1. But if chloride of ammonium be present, the process becomes less accurate. When compounds of aluminum and iron are ignited with chloride of ammonium, a certain amount of chloride of aluminum or of chloride of iron, as the case may be, is lost through volatilization. Under like circumstances manganese

compounds are converted into protochloride of manganese mixed with some manganite of manganese; zinc compounds volatilize as chloride of zinc, and compounds of cobalt and nickel are reduced to the metallic state. The safest rule in all these cases is to mix the sample with carbonate of sodium before igniting it, and to determine the metals in the residue by some appropriate process. The ammonia may then be estimated in a separate portion of the mixture by distillation with an alkali. (See Ammonia).

Ammonio-Sesquioxide of Uranium.

See Oxide of Uranium (ammoniated).

Antimonic Acid.

Principle I. Sparing solubility in nitric acid.

Applications. Separation of antimony from Mg, Zn, Cd; Mn, Fe, Co, Ni; Bi, Cu, Hg, Ag and Pb in alloys.

Method. Dissolve the alloy in nitric acid or in aqua regia, as described under *bin*Oxide of Tin. Collect the insoluble residue of antimonious acid upon a filter and ignite to convert it into Antimoniate of Antimony. The results are only approximative, since a small portion of the antimony always remains dissolved in the acid. Alloys of lead and antimony, containing a large proportion of antimony, should be fused with a weighed quantity of pure lead before treating them with nitric acid, lest a part of the alloy escape solution. — According to Pfaff (*Handbuch analyt. Chem.*, 1825, 2. 416), the antimonious acid is apt to retain a certain quantity of oxide of lead, so firmly combined that it does not dissolve in nitric acid.

This process was formerly much employed for analyzing antimony alloys, and is still used for technical analyses, where no great accuracy is required. It is now recognized, however, that—owing to the solubility of antimonious acid in nitric acid—the process yields far less accurate results than the corresponding method with Oxide of Tin. By repeatedly evaporating the nitric acid solution of antimonious acid to dryness, and treating the residue again and again with fresh portions of nitric acid, it is indeed possible to obtain at last a solution free from antimonious acid, but the operations require so much time that they are not employed in actual practice.

Principle II. Power of changing stannous to stannic chloride, while it is itself reduced to the state of antimonious acid.

Applications. Estimation of antimony in cases where the metal can be converted into antimonious acid.

Method. Mix a weighed quantity of the antimonious acid with a measured volume of a standard solution of protochloride of tin, together with some iodide of potassium solution and starch paste. The quantity of the tin solution must be more than sufficient to reduce

the whole of the antimonious acid, and the mixed solution must be heated to 40°. Finally determine how much stannous chloride remains in the solution, by means of a standard solution of *bi*Chromate of Potassium. The process is of limited application, and is said not to yield very accurate results. (See Chloride of Tin).

Antimoniate of Antimony.

(Improperly "Antimonious Acid").

Principle. Fixity of the compound when heated.

Applications. Estimation of antimony in antimonious and antimonious acids, and in compounds of these acids with easily volatile or decomposable oxygenated acids or bases. Determination of antimony in sulphide of antimony.

Method. Antimonious acid may be simply ignited in a platinum crucible until the weight remains constant. Other compounds of antimony should be treated with nitric acid free from chlorhydric acid, and the solution carefully evaporated to dryness before igniting them. Care must be taken to guard the contents of the crucible against the action of reducing gases coming from the filter or the flame.

For converting sulphide of antimony into antimoniate of antimony, Bunsen* has devised two methods, as follows:—

1. *With fuming Nitric Acid.* Place the dry sulphide in a weighed porcelain crucible, moisten it with a few drops of nitric acid of 1.42 specific gravity, and cover the crucible loosely with a watch glass or small funnel from which the tube has been cut away. Carefully pour upon the sulphide 8 or 10 times its bulk of red fuming nitric acid, place the crucible on a water bath and allow the acid to evaporate slowly. When the nitric acid is first added to the sulphide, a quantity of sulphur separates in fine powder, but subsequently oxidizes completely during the process of evaporation, so that nothing but a white mixture of antimonious and sulphuric acids is left in the crucible. By igniting this residue it is converted into antimoniate of antimony. — In case the sulphide of antimony under examination happens to be mixed with a large proportion of free sulphur, it must be washed with bisulphide of carbon before adding the nitric acid. The washing may be effected as follows:—By means of a perforated cork, fit the funnel which contains the filter and the dried sulphide of antimony, air tight to the mouth of a test tube; pour enough sulphide of carbon into the filter to cover the dry precipitate, then cover the funnel tightly with a glass plate, and leave the apparatus at rest for several hours. Finally loosen the cork and allow the bisulphide of carbon to flow into the test tube. Repeat the operation, if need be, with a fresh quantity of bisulphide of carbon; 10 or 15 grms. of the bisulphide will, in most cases, be enough for washing a single precipitate; it may always be

easily recovered by distillation and kept for future use.

It is to be observed that *fuming* nitric acid is essential to the success of this process. The ordinary strong nitric acid of 1.42 specific gravity will not answer. The boiling point of the acid of 1.42 specific gravity is almost 10° higher than the melting point of sulphur, while the fuming acid boils at a temperature as low as 86° , far below that at which sulphur melts. The hot fuming acid easily oxidizes the finely divided sulphur with which it is in contact, but when heated with acid of 1.42 specific gravity, the particles of sulphur quickly melt to a solid ball, which obstinately resists oxidation.

No chlorhydric acid should be present lest some of the antimony be lost through volatilization of the terchloride when the dry mass is ignited.

2. *By Ignition with Oxide of Mercury.* Mix the sulphide of antimony with from 30 to 50 times as much precipitated oxide of mercury, and heat the mixture gradually in an open weighed porcelain crucible. Remove the lamp as soon as the appearance of gray fumes of mercury indicates that oxidation has begun. Again heat the mixture as soon as the fumes slacken, and proceed in this way as long as fumes are evolved. Finally ignite the crucible over a blast lamp to remove the last traces of oxide of mercury, and weigh the residual antimoniate of antimony.

Care must be taken that no reducing gases from the lamp gain access to the contents of the crucible. Since oxide of mercury always leaves a small quantity of fixed residue, even after intense ignition, it is well to determine the proportion of this impurity once for all, to weigh roughly the amount of oxide of mercury taken to oxidize any sample of the sulphide, and to subtract the amount of fixed residue contained in the oxide of mercury taken from the weight of the antimoniate of antimony.

If the sulphide of antimony is mixed with free sulphur, this sulphur must be removed by means of bisulphide of carbon, as in No. 1, in order to avoid slight deflagrations and consequent loss of substance, which would otherwise occur when the sulphide came to be heated with oxide of mercury.

The operation may be completed much more quickly in a platinum than in a porcelain crucible. But if a platinum crucible be employed it must be protected from the action of antimony by means of a lining of oxide of mercury. This lining may be made as follows:— Soften the end of a test tube at the blast lamp, place the soft end of the tube in the centre of the platinum crucible, and blow air into the other end of the tube, so that the hot glass may assume the exact form of the crucible. Crack off the bottom of the bulb thus formed, and carefully smooth the sharp edge by fusion. A glass is thus obtained, open at both ends,

which exactly fits the crucible. Fill the crucible loosely with oxide of mercury to the brim, and slowly push the glass through the mercury to the bottom of the crucible, occasionally shaking out the oxide from the interior of the glass. A layer of oxide of mercury from half a line to a line thick, may thus be pressed against the crucible so firmly that it will adhere to the platinum after the removal of the glass.

Properties. Antimoniate of Antimony is a white powder when cold, but exhibits a yellowish tint while hot. It neither fuses nor decomposes when ignited in the air. It is scarcely at all soluble in water, though it exhibits an acid reaction when placed upon moist litmus paper. It is not acted upon by sulphhydrate of ammonium, and dissolves in chlorhydric acid with very great difficulty. Its composition is:—

$$\begin{array}{rcl} \text{Sb} & = & 122 = \frac{80.26}{.82} \\ \text{O}_2 & = & 32 = \frac{19.74}{.154} \\ & & 154 \quad 100.00 \end{array}$$

Antimoniate of Mercury.

(Mercurous antimoniate).

Principle. Insolubility in water.

Applications. Separation of antimony from potassium and sodium.

Method. Mix the solution of the antimoniate with an excess of a solution of nitrate of suboxide of mercury. Allow the mixture to stand at rest for many hours, collect the precipitate upon a filter, wash with a solution of mercurous nitrate, dry, ignite strongly, and weigh as Antimoniate of Antimony. Remove the excess of mercury from the filtrate by means of sulphuretted hydrogen or chlorhydric acid, and determine the alkalies in the final filtrate in the usual way. — Antimoniate of mercury, as formed by the mixture of mercurous nitrate and antimoniate of potassium or sodium settles with extreme slowness, but the mixture may nevertheless be filtered without special difficulty, if it be first allowed to stand for a long time.

Antimoniate of Sodium.

Principle. Insolubility in dilute alcohol.

Applications. Separation of antimony from arsenic and tin.

Methods.

1. Place the substance to be analyzed, which may be an alloy of antimony, arsenic and tin, or a mixture of sulphide of antimony and sulphide of tin, in a large beaker, and pour upon it, little by little, nitric acid of 1.4 specific gravity, until the oxidation is completed; an alloy should be reduced to the state of fine powder before weighing. For an alloy, the nitric acid employed must be of the prescribed strength, since acid of 1.52 specific gravity would not attack the alloy; but for the treatment of sulphides the stronger acid is to be preferred. When the reaction has ceased to be violent, transfer the mixture from the beaker to a small porcelain dish, evaporate to dryness

on a water-bath, transfer the residue to a silver crucible, rinse out the porcelain dish with a solution of caustic soda, and again evaporate to dryness. Add to the contents of the crucible as much solid hydrate of sodium as will amount to about eight times the bulk of the residue, and fuse the mixture for some time at a red heat. When the crucible has become cold, cover the fused mass with water, and allow it to soak until it softens, then wash out the contents of the crucible into a beaker, with hot water, and continue to add water until the undissolved residue has assumed the form of a fine powder. Stannate and arseniate of sodium go into solution while most of the antimoniate of sodium remains undissolved. Add to the solution in the beaker as much alcohol of 0.83 specific gravity as will amount to about one-third the volume of the solution. Cover the beaker with a glass plate, and let the mixture stand for 24 hours with frequent stirring. Collect the insoluble matter in a filter, rinse the beaker with spirit made by mixing 1 vol. of alcohol of 0.83 specific gravity with 3 vols. of water, and wash the precipitate upon the filter, first with a mixture of 1 vol. alcohol and 2 vols. water, then with a mixture of equal volumes of alcohol and water, and finally with a mixture of 3 vols. alcohol and 1 vol. water. It is well to mix a few drops of a solution of carbonate of sodium with the dilute alcohol used for washing. The carbonate facilitates the solution of the stannate of sodium, and hinders the antimoniate of sodium from passing through the pores of the filter. — Continue to wash until a portion of the filtrate acidified with chlorhydric acid and mixed with sulphuretted hydrogen water gives no yellowish precipitate of sulphide of tin after long standing.

It is essential that the alcohol used for washing shall be of the prescribed strengths. If strong alcohol were used at first, a quantity of carbonate of sodium formed during the fusion would be left undissolved upon the filter, and would retain stannate of sodium in combination, to such an extent as to occasion losses even as great as 8 or 9 per cent. Weak alcohol, on the other hand, dissolves some antimoniate of sodium, together with the stannate. Water alone cannot be employed for the washing. Not only is antimoniate of sodium somewhat soluble in water, but a portion of the precipitate itself would pass through the pores of the filter as soon as the stannate and carbonate of sodium had been washed away, if nothing but water was employed.

When the antimoniate of sodium has been thoroughly washed, rinse it from the filter into a beaker, leach the paper with a mixture of chlorhydric and tartaric acids, dissolve the precipitate in the same mixture of acids, and precipitate the antimony as Sulphide of Antimony. The antimoniate of sodium cannot be weighed directly, since, though free from stan-

nate of sodium, it always retains some carbonate or sulphate of sodium when washed as above directed. — The process yields excellent results when properly conducted. The antimoniate of sodium settles completely from the alcoholic solution, and the latter is easily filtered. The only real inconvenience arises from the necessity of using a silver crucible, and the consequent liability of contaminating the alkaline filtrate with a small amount of silver.

To determine the tin and arsenic in the filtrate, acidulate the liquid with chlorhydric acid, and without heeding the precipitate of stannic arseniate which forms, pass sulphuretted hydrogen gas for some time through the turbid liquid. Allow the mixture to stand until the odor of sulphuretted hydrogen has well nigh disappeared, collect and weigh the mixture of sulphide of tin, sulphide of arsenic and free sulphur upon a tared filter, and finally heat a portion of the precipitate in a current of hydrogen to expel the sulphur and Sulphide of Arsenic.

If there be no arsenic, but only tin in the filtrate, drive off most of the alcohol by evaporating at a gentle heat, dilute with water and supersaturate with sulphuric acid to precipitate Hydrate of Tin. Or precipitate Sulphide of Tin. The precipitation with sulphuretted hydrogen is safer than the other process, though the sulphide of tin will be contaminated with a trace of sulphide of silver from the crucible, while by using sulphuric acid no compound of silver is thrown down.

In case there be no tin, but only antimony and arsenic is the substance to be analyzed, the arsenic may be determined as Arseniate of Magnesium and Ammonium. To this end, heat the alcoholic filtrate, with the addition of several fresh quantities of water, until the odor of alcohol has almost disappeared, acidulate with chlorhydric acid and proceed in the usual way.

2. In the case of mixtures of the sulphides of arsenic and antimony, together with free sulphur, such as are often obtained in mineral analyses, the process may be modified, as follows:—Place the precipitate in a porcelain crucible, oxidize it with red fuming nitric acid free from chlorine, evaporate nearly to dryness, mix the residue with an excess of carbonate of sodium, together with some nitrate of sodium, and fuse at the lamp. Treat the fused mass as directed in No. 1.

Antimonious Acid, (Sb_2O_3). [For the compound Sb_2O_4 —sometimes improperly called antimonious acid, see Antimoniate of Antimony.]

Principle I. Oxidation by Iodine (A) or by Chlorine (B) in alkaline solution; by Bichromate (C) or Permanganate of Potassium (D), or by Salts of Gold (E).

The Applications of A, C, and D, are limited to the estimation of antimonious acid in

pure solutions of this substance—such as the chlorhydric acid solution of sulphide of antimony and, as regards A and D, a solution of tartar-emetic—and to the determination of antimonious acid when mixed with antimonie acid. The applications of B will appear below under the head of Antimony.

Methods. To separate antimonious from antimonie acid, determine the total amount of antimony in one portion of the substance to be analyzed, by precipitation of Sulphide of Antimony. Determine the amount of antimonie acid, in another portion, by one of the processes enumerated below, and calculate the amount of antimonie acid from the difference.

A. Weigh out as much of the substance to be tested as will contain about 0.1 gm. of antimonious acid. Dissolve the weighed substance in 10 or 12 c. c. of a strong aqueous solution of tartaric acid, in case it be not already a tartrate, and add enough carbonate of sodium solution to nearly neutralize the liquid. Mix the solution with 20 c. c. of a cold saturated solution of bicarbonate of sodium, add a few c. c. of thin starch paste, and pour into the mixture, drop by drop, from a burette, a standard solution of iodine in iodide of potassium until the liquid just remains blue, or better, is of a faint red color. The mixture must of course be stirred continually while the iodine solution is being added to it:—



So long as there is any antimonious acid present to be oxidized, the blue color formed at the surface of the liquor where the iodine solution first touches the starch, will be destroyed as fast as it forms. But as soon as the last trace of antimonious acid is oxidized, the whole solution will become blue. The operation must be stopped at this moment. The blue color will, in any event, disappear after a few minutes. The value of the iodine solution may be determined beforehand by titrating 0.2 or 0.3 gm. of pure crystallized tartar emetic. (Mohr, *Titrirmethode*, 1855, p. 371).

Though the results obtained by this process are, on the whole, satisfactory, it is, according to Fresenius, essential that the proportion of antimonious acid to that of bicarbonate of sodium be maintained tolerably near that of the quantities above enumerated, in order to ensure accuracy. Bicarbonate of sodium should always be employed as the alkaline liquor, since the monocarbonate has the power of fixing a certain amount of iodine.

Instead of titrating directly with a solution of iodine, as above described, H. Rose directs that the standard solution of iodine be added to the slightly alkaline solution of antimony as long as its color continues to be discharged, and that the excess of iodine be then determined with a standard solution of Hyposulphite of Sodium.

B. *Oxidation by Chlorine.* Same as under Antimony.

C. *Oxidation by Bichromate of Potassium.* To the solution of antimonious acid in diluted chlorhydric acid, add a measured volume of a standard solution of bichromate of potassium, more than sufficient to oxidize the whole of the antimony. Leave the mixture at rest for a short time, and finally determine the amount of unoxidized chromate by means of a standard solution of ferrous sulphate, added until a drop of the mixture gives a blue precipitate when touched to a drop of ferricyanide of potassium. (See *biChromate of Potassium*). The original chlorhydric acid solution should contain at least one-sixth its volume of chlorhydric acid of 1.12 specific gravity. It will often be found convenient in practice to operate with solutions composed of about equal volumes of water and chlorhydric acid, but in case more acid than this is present, the delicacy and promptitude of the final reaction with ferricyanide of potassium is materially diminished. As with arsenious acid, bichromate of potassium does not act upon antimonious acid in any definite or reliable way when the solution in which the oxidation is to be effected contains less than one-sixth its volume of chlorhydric acid. Since tartaric acid decomposes the bichromate, its presence is inadmissible.

If the substance to be analyzed is free from organic matter, oxides of the heavy metals, and other substances capable of interfering with the titration, it may be dissolved at once in chlorhydric acid; otherwise the antimony must be precipitated, in the first place, as a Sulphide. To prepare the sulphide for titration, place the washed precipitate, together with the filter, in a small flask, cover it with chlorhydric acid, heat the mixture on a water bath until the precipitate has dissolved, add to the liquid as much of a nearly saturated solution of mercuric chloride in chlorhydric acid of 1.12 specific gravity as may be needed to remove the sulphuretted hydrogen, dilute the mixed solution to some definite volume, allow it to settle, and take up a measured volume of the clear liquid for the analysis. (Kessler, *Poggendorff's Annalen*, 95. 215; 113. 134; and 118. 17).

D. *Oxidation by Permanganate of Potassium.* Pour a standard solution of permanganate of potassium from a burette into the chlorhydric acid solution of antimonious acid, until the solution exhibits a permanent red color. The permanganate solution should contain about 1.5 gm. of the crystallized salt to the litre, and the antimony solution at least one-sixth its volume of chlorhydric acid of 1.12 specific gravity. It is not well, however, to have the proportion of acid higher than one-third the volume of the liquid, since the final reaction would be interfered with. The

presence of tartaric acid has little or no influence upon the reaction. Hence the process may be employed for analyzing tartar emetic, and the value of the permanganate solution may be determined in the beginning by means of a standard solution of pure tartar emetic.

For the preparation of the antimony solution see above, C. (Kessler, *Poggendorff's Annalen*, 118. 17).

E. Oxidation by Salts of Gold. A process formerly recommended by H. Rose consisted in mixing the antimonious acid, dissolved in a very large excess of strong chlorhydric acid, with an excess of chloraurate of sodium or chloraurate of ammonium, leaving the mixture at rest during several days at a temperature slightly warmer than that of the air, and collecting and weighing the metallic gold which was deposited, as was supposed, in quantity proportionate to the amount of antimonious acid in the solution. But since Dexter (*Pogg. Ann.*, 100. 570; compare H. Rose, *ibid.*, 110. 541) has shown that the process affords neither concordant nor reliable results, it can no longer be commended.

Principle II. Volatility.

Method. To separate antimony from silver, gold, and other noble metals, the alloy may be heated upon a cupel in a muffle. By the action of the hot air the antimony will be converted into antimonious acid, and the latter will go off in the form of vapor, leaving the silver or gold to be weighed. It has been found in practice that a simple alloy of silver and antimony heated upon bone ash in a muffle, until fumes of antimonious acid are no longer visible, still retains about one per cent of antimony, the residual button of silver being dull and gray, and only incompletely soluble in nitric acid. But by again heating the button on a cupel with about 5 times its weight of lead, until the lead has all been oxidized and the melted silver appears bright and lustrous, the antimony may be completely expelled.

Antimony. [Compare Antimony Compounds].

Antimony is estimated as metallic Antimony, as Sulphide of Antimony, Antimoniate of Antimony, Antimoniate of Sodium, or by titration, as has been explained under Antimonious Acid. See also Antimonic Acid, and the finding list in Appendix.

Principle I. Sparing solubility of the metal in chlorhydric acid.

Applications. Estimation of antimony in antimony salts. Separation of antimony from tin.

Method A. Precipitate the antimony by means of metallic zinc from a dilute nitric acid solution. The antimony falls as a black powder, which glistens when burnished. (Pfaff, *Handbuch analyt. Chem.*, 1825, 2. 411). So long as zinc is present in the liquid the antimony suffers no oxidation or solution. Wash

rapidly with hot water and dry at 100°, best in an atmosphere of non-oxidizing gas. — To separate antimony from tin, boil the alloy with chlorhydric acid [taking care to absorb any antimoniucretted hydrogen that is evolved (see below, Method D.)] until all the tin has dissolved, then place a rod of pure tin in the liquor to precipitate any traces of antimony which may have dissolved, and proceed as before. (Pfaff, *loc. cit.*, p. 416).

Method B. To analyze an alloy of tin and antimony, dissolve it completely in chlorhydric acid to which a little nitric acid has been added. Heat the solution nearly to boiling, and throw into it bits of fine iron wire (piano-wire), as long as the latter continues to dissolve. As soon as all the antimony has been precipitated, and the last piece of iron seems to have completely dissolved, add a little more chlorhydric acid; allow the precipitate to settle, decant the clear liquid, and try whether any further precipitate can be produced in it by means of iron. Wash the precipitated antimony at first with hot water acidulated with chlorhydric acid, afterwards with pure hot water, and finally with strong alcohol. To facilitate the operation of drying, and to still further guard against the risk of oxidation, it is well to wash out the alcohol with a few drops of ether. Dry the precipitate quickly at 100°, and weigh. — The process yields good results when the proportion of tin is large, but is less accurate when the solution contains but little tin. (Tookey & Clasen, *Zeitsch. analyt. Chem.*, 1865, 4. 440).

Method C. Place the alloy or other compound in a small flask, cover it with strong chlorhydric acid, heat the mixture and add small crystals of chlorate of potassium, one by one, until the solution is complete. Dilute the liquid to some definite volume, and divide it into two equal parts. In one part precipitate both the antimony and the tin on a rod of metallic zinc and wash, dry and weigh the powder. Mix the other part with a tolerably large quantity of chlorhydric acid, place a clean strip of metallic tin in the liquid and heat the whole gently for some time. All the antimony will be precipitated while the tin is reduced to the condition of stannous chloride. Wash the precipitate with water acidulated with chlorhydric acid, collect it on a tared filter, dry and weigh. The difference in weight between the first and second precipitates gives the amount of tin. — In case the substance to be examined contains nothing but antimony and tin, the first precipitation with zinc may be omitted, and the difference between the weight of alloy taken and that of antimony found may be regarded as the weight of the tin. Since antimony is not completely precipitated by tin at the ordinary temperature, unless, indeed, after a long time, it is necessary to keep the liquid at a temperature slightly higher than that of the air during the precipitation.

The liquid should contain an excess of acid also from first to last. (Gay-Lussac).

As a modification of Gay-Lussac's process, Levol precipitates the antimony and tin together upon a zinc rod, rinses off the metallic powder which adheres to the zinc when the precipitation is complete, and, without decanting the solution of chloride of zinc, treats the mixed precipitate of tin and antimony with strong chlorhydric acid in order to dissolve the tin. He then weighs the antimony and determines the tin in the filtrate, as Sulphide of Tin. In reply to the criticism of Elsner that this method is inexact, inasmuch as strong chlorhydric acid dissolves some of the antimony as well as the tin, Levol remarks that in presence of chloride of zinc the action of the acid upon antimony is materially lessened. The method can hardly be expected, however, to afford very accurate results in any event.

Method D. A third modification of the process, applicable to cases where the proportion of antimony in the alloy is small, is the following:—Fit to a small flask a cork carrying a thistle tube and two other short tubes, each bent at a right angle. Put the finely divided alloy in the flask, replace the cork, and connect one of the delivery tubes with a source of carbonic acid, and the other with several U-tubes charged with small quantities of red fuming nitric acid free from chlorine. Pour enough strong chlorhydric acid into the flask to seal the thistle tube, and heat the mixture gently. The tin will dissolve completely, and most of the antimony remain in the metallic state, though a part of it goes off in the form of antimoniu-retted hydrogen gas. This gas will be oxidized, however, and the antimony retained by the nitric acid in the U-tubes. When the alloy has dissolved, dilute the contents of the flask to some definite volume with recently boiled water, allow the mixture to settle and determine the tin in a measured volume of the clear liquor. Then filter the rest of the liquid, wash the precipitate with acidulated water, place it in a porcelain crucible, add to it the contents of the U-tubes, evaporate to dryness and weigh as Antimoniate of Antimony. If the alloy contain arsenic as well as antimony, the residue obtained by evaporating the contents of the U-tubes would be treated, with the metallic precipitate, as is explained under Antimoniate of Sodium.

Method E. One of the oldest of the processes dependent on the principle now in question, is that of Chaudet (H. Rose, *Handbuch*, 1865, 2. 301). In this process the antimony is kept in contact with a large proportion of stannous chloride in order that the solvent action of the chlorhydric acid upon the antimony may be hindered. After having determined that the alloy contains nothing but antimony and tin, the first step is to ascertain, approximately, the relative proportions of the two metals. To this end melt one part of the alloy

with about 20 parts of metallic tin, roll the product to a sheet, and boil it for a long time with strong chlorhydric acid. The weight of the undissolved matter, after drying, will indicate very nearly the proportion of antimony in the alloy. Next melt very carefully a new portion of the alloy with pure tin, taken in such proportion that there shall be in the melted product 20 parts of tin to 1 of antimony. The weighed metals should be wrapped in paper, placed in a small Hessian crucible, covered with powdered charcoal to prevent oxidation, and ignited for ten minutes in a hot fire. After the crucible has cooled, brush the metallic globule, beat or roll it to a sheet, cut the sheet metal into several pieces, roll the pieces in paper as before, place them in a crucible, cover with powdered charcoal and melt during another space of ten minutes in order to obtain a thoroughly homogeneous alloy. Brush the new globule, roll it to a thin sheet and cut the product into a number of pieces. Weigh out a quantity for analysis, place it in a flask, cover it with strong chlorhydric acid and boil the acid during at least two and a half hours. Dilute the acid with water, collect the finely divided antimony on a weighed filter, dry and weigh. The tin in the original alloy is estimated from the difference. As far as the estimation of antimony is concerned the presence even of a large proportion of lead in the original alloy does no harm.

Properties. Precipitated antimony is a dull black powder, which may be dried at 100° without alteration. It fuses at a moderate red heat. When strongly ignited in hydrogen gas a small part of it volatilizes without chemical change. Nitric acid oxidizes it with formation of antimonious acid, mixed with more or less antimonious acid, according to the strength of the nitric acid. Chlorhydric acid acts upon it but slowly, though an appreciable quantity of it dissolves when left in contact with the acid for several days in open vessels. Dilute acid dissolves more of it than concentrated, and cold acid more than the same acid when boiling. Acid charged with stannous chloride has little or no action upon it.

Principle II. Oxidation by chlorine in alkaline solutions (Method A), by aqua regia, or a mixture of chlorate of potassium and chlorhydric acid (Method B), or by hot air (Method C).

Applications. Separation of Sb from As (B and A); of Sb from Cu and Fe, especially in ores containing sulphur, and from Co and Ni; (Method A). Separation of Sb from Ag, Au and other noble metals. (Method C).

Method A.

1. *To separate Sb from Cu and Fe in sulphuretted ores.* Reduce the mineral to very fine powder, diffuse it through a solution of caustic potash free from sulphuric acid, heat the liquor and pass chlorine gas through it for sev-

eral hours. The sulphur oxidizes rapidly, copper and iron are deposited as oxides and a solution of sulphate and antimoniate of potassium obtained. Antimony may be estimated in the filtrate as Sulphide of Antimony. (Rivot, Beudant & Daguin, *Comptes Rendus*, 1853, 37. 835).

2. To separate Sb from As. Oxidize the mixture with chlorine as in No. 1, and remove the arsenic by precipitation, as Arseniate of Magnesium and Ammonium. Finally determine the antimony as Sulphide.

3. To separate Sb from Co and Ni, add to the dilute nitric acid solution of the three metals a large excess of caustic potash, heat the mixture gently and pass chlorine gas into the mixture until the precipitate is black. The precipitate contains the cobalt and nickel as sesquioxides, while the antimony remains in solution as antimoniate of potassium as in No. 1. (Rivot, etc., *loc. cit.*)

Method B. Oxidize the mixed metal or sulphide by boiling with aqua regia, or with chlorhydric acid to which crystals of chlorate of potassium are frequently added, and remove the arsenic acid by precipitation as Arseniate of Magnesium and Ammonium. Determine the antimony in the filtrate as Sulphide.

Method C. See Antimonious Acid, (volatility of).

Antimony Compounds.

Principle I. Reduction of to the metallic state by hydrogen.

Applications. Estimation of antimony in the sulphide or in any other compound of antimony.

Method. Weigh out a small quantity of the dry sulphide, or other compound of antimony to be tested, in a weighed bulb-tube of hard glass; connect the tube with a hydrogen generator and pass a slow stream of dry hydrogen through the tube. Heat the antimony compound, gently at first, until the compound is wholly reduced and the sulphur or other sublimate has been completely expelled from the tube. Remove the lamp and continue the current of hydrogen until the tube is cold, then hold the tube nearly upright for a moment to fill it with air and weigh it together with the antimony which it contains. A minute quantity of antimony is apt to be carried forward either as antimoniretted hydrogen, or through volatilization of sulphide of antimony, in the current of gas, but most of it may be recovered by heating the narrow part of the tube to redness with a second lamp placed beyond the bulb. A mirror of metallic antimony will be deposited near this second lamp, on the walls of the tube. When the operation is carefully conducted the loss of antimony through volatilization is so small that it hardly amounts to a quarter of one per cent of the total weight of the antimony, even if no second lamp be employed, but it is easy to drive off half a per cent or more by careless heating. The matter

in the bulb should never be heated intensely, until the reduction is deemed to be well nigh finished.

Principle II. Reduction of to metallic antimony by iron, zinc or tin. See Antimony, sparing solubility of in chlorhydric acid.

Arsenic Acid.

Principle I. Reduction of by sulphur.

Applications. Estimation of arsenic, by loss, in many metallic arseniates. Separation of Fe, Mn, Zn, Pb and Cu from arsenic acid.

Method. Mix the powdered arseniate with pure, powdered sulphur in a porcelain crucible (Rose's reduction-crucible is best) and ignite the mixture in a slow stream of hydrogen gas. The arsenic acid is reduced to metallic arsenic and sulphide of arsenic, which escape in the form of gas, while the metal to be separated from the arsenic remains in the crucible, and is weighed as a sulphide. The apparatus must be so arranged that the arsenic fumes may be carried either into a chimney or into the open air. A simple ignition of the arseniate with sulphur in a covered crucible would be sufficient in most cases to complete the reduction of the arseniate and to expel all the arsenic, but the residual sulphide would then be left in an impure condition. The purpose of the current of hydrogen is to ensure the removal of any excess of sulphur from the residual sulphide.

In case the substance to be analyzed has been thoroughly mixed with sulphur, a single ignition will complete the transformation of the arseniate to a sulphide, but it is always well, after weighing, to mix the residue with a fresh quantity of sulphur and to ignite a second, or if need be, a third time until the results of two consecutive weighings are the same. In order that the amount of arsenic may be determined by the loss, the substance to be analyzed should be made anhydrous by heating it nearly to redness, before weighing, though the reaction with sulphur would take place with an air-dried arseniate as well as with one which had been ignited. The crucible employed must not only be of porcelain but must be provided with a porcelain cover; a platinum cover will not answer since the arsenic fumes would quickly render it brittle and friable. (H. Rose, *Zeitsch. analyt. Chem.*, 1862, 1. 413).

Principle II. Reduction of by chloride or sulphate of ammonium.

Applications. Estimation of arsenic, by loss. Separation of Na, K, Ba, and other metals from arsenic acid.

Method A. With Chloride of Ammonium. Mix the finely powdered arseniate with from 5 to 8 times its weight of chloride of ammonium and heat the mixture in a covered porcelain crucible until the weight of the residue remains constant. Arseniates of the alkali metals are easily reduced in this way to the condition of chlorides. So, too, is arseniate of barium, though far less easily than the alkaline arsen-

iates; but arseniate of magnesium cannot be completely reduced. The arseniates of iron, cobalt and nickel heated with chloride of ammonium in a stream of hydrogen yield metallic iron, cobalt or nickel, as the case may be, but the product is mixed with so much arsenic that no useful information can be obtained by weighing it. Arseniate of copper is reduced to metallic copper free from arsenic, but during the ignition a quantity of chloride of copper escapes in the form of gas. The process yields really useful results with arseniates of the alkali-metals alone. (H. Rose, *Pogg. Ann.*, 73. 582; 74. 562; further *Zeitsch. analyt. Chem.*, 1862, 1. 422).

Method B. With Sulphate or Acid Sulphate of Ammonium. According to Finkener, acid sulphate of ammonium decomposes many arseniates far more quickly and completely than chloride of ammonium. Though the process, in its present condition, is of no value to the analyst, it is nevertheless worth describing, in the hope that it may be improved. Melt in a porcelain crucible 7 or 8 times as much acid sulphate of ammonium as there is arseniate to be decomposed, and add the latter, little by little, in fine powder to the melted salt. Finally heat the mixture until the excess of ammonium salt has all been driven off and weigh the metallic sulphate which remains in the crucible. It would not be well to heat the mixture of the ammonium salt and arseniate directly, since the mixture would froth violently as it became fluid and some of it would be thrown out of the crucible. Normal sulphate of ammonium can be used instead of the acid salt, though the arsenic is rather more readily expelled by the latter. The process would be valuable, were it not that the crucible is strongly acted upon by the melted ammonium salt in such manner that the metallic sulphate to be weighed is contaminated with other sulphates, formed by the union of sulphuric acid with the ingredients of the crucible, to such an extent that the results are usually much too high. (H. Rose, *Zeitsch. analyt. Chem.*, 1862, 1. 423).

Principle III. Reduction of by cyanide of potassium. See Arsenic, volatility of.

Principle IV. Solubility in alcohol.

Applications. Separation of arsenic acid from most of the arseniates. The arseniates of iron and aluminum seem to be less easily analyzed in this way than most other arseniates. The magnesium salt, on the other hand, has been thus analyzed with great exactitude.

Method. Mix the arseniate to be analyzed with concentrated sulphuric acid in a platinum dish, and keep the mixture slightly warm until it forms a thick syrup. Add to the syrup a quantity of solid sulphate of ammonium equal to that of the arseniate taken and again heat the mixture until most of the excess of sulphuric acid has been expelled. Allow the mixture to cool and dissolve the viscous mass in the least

possible quantity of water, with the aid of gentle heat. Pour upon the solution a large excess of alcohol of 0.83 sp. gr., cover the dish which contains the mixture and leave it at rest for 12 hours. Insoluble double sulphates of ammonium and of the metals to be separated are deposited as fine crystalline powders, while the arsenic acid and the excess of sulphuric acid dissolve in the alcohol. Collect the precipitate upon a filter, wash it with alcohol, dry, ignite to drive off sulphate of ammonium and weigh the residual sulphate of —, or, in case it cannot be ignited without decomposition, determine the metal in some appropriate way. The arsenic acid may be estimated from the loss or as Arseniate of Magnesium and Ammonium, after diluting with water and expelling the alcohol.

The mixture of sulphate of ammonium and sulphuric and arsenic acids must be dissolved in water before adding the alcohol, or a hard mass will be formed impermeable to alcohol. After the alcoholic mixture has stood 12 hours, ether may be added to it to ensure the precipitation of any traces of sulphates which the alcohol may have dissolved; though as a rule the addition of the ether is not necessary.

Basic Arseniate of Iron (Ferrio Arseniate).

Principle. Insolubility in water and fixity when heated.

Applications. Estimation of arsenious and arsenic acids in solutions free from other substances precipitable by ammonia-water, by sesquichloride of iron, on addition of ammonia-water, or by carbonate of barium. Separation of arsenic from Li, Na, K; Ba, Ca, Sr; Zn, Mn, Ni and Co.

Method A. The substance to be analyzed contains no non-volatile metals besides alkali-metals. (Berthier's method). Mix the solution which contains the arsenic acid with a measured quantity of a standard solution of nitrate of sesquioxide of iron and add ammonia-water to the mixture until a decided odor of ammonia persists. In case the substance to be examined contains arsenious acid, it must first be treated with aqua regia, or with nitric acid and chloride of potassium, to convert the arsenious acid into arsenic acid. If the precipitate produced by ammonia is not of a reddish-brown color another measured portion of the standard iron solution must be added, and afterwards enough ammonia-water to make the solution alkaline. After the mixture has stood for some time at a gentle heat, collect the precipitate upon a filter, wash it with water and allow it to dry. Place the dry precipitate together with the filter ash in a platinum crucible, and heat it very gently for some time in order to expel ammonium compounds at a temperature lower than that at which they can reduce arsenic acid. Increase the heat gradually and at last ignite the crucible intensely. The substance weighed is arsenic acid plus sesquioxide of iron, but the

weight of the latter is known from the quantity of the standard iron solution taken. Hence we have only to deduct the weight of ferric oxide taken from the weight of the ignited precipitate to obtain the amount of arsenic acid contained in the substance analyzed.

The best way of making the standard iron solution is to dissolve fine iron wire (piano wire) in hot nitric acid, to dilute the liquid to some definite volume (see Alkalimetry), and then to determine how much sesquioxide of iron is contained in 10 c. c. of the liquid, by precipitation with ammonia-water (see Hydrate of Iron). In this case the presence of a small amount of silica or other precipitable impurity in the iron does no harm, since it is weighed with the oxide of iron both when the strength of the iron solution is determined and in the final arsenic estimation. (Berthier).

Precautions. The process is applicable with sulphuric acid solutions as well as with solutions charged with nitric or with chlorhydric acid, but when sulphuric acid is present it is well to ignite the crucible and precipitate a second time or even a third time after weighing, until the weight remains constant, in order to be sure that all the sulphuric acid has been expelled. This precaution is doubly necessary since it would here be inadmissible to employ carbonate of ammonium (as is done with Sulphate of Potassium), to remove the last traces of sulphuric acid. In case chlorhydric acid is present, the last traces of chloride of ammonium must be washed out of the precipitate lest some of the iron be volatilized as sesquichloride, on ignition. In any event the precipitate must be cautiously heated. If the dry precipitates were strongly ignited at once without any preliminary warning, some of the arsenic acid would be reduced to the condition of arsenious acid or even to metallic arsenic by the action of ammonium compounds contained in the precipitate, and the residue would weigh less than it ought. Even with the most careful heating a small amount of material is usually lost. Besides this liability to loss through reduction of the arsenic acid, an objection to the process is found in the fact that it is sometimes very hard to wash the precipitate completely, and that the last portions of wash water are apt to dissolve some arseniate of iron, in which event the wash water acquires a faint reddish color. This difficulty may be avoided, however, by washing with dilute ammonia-water.

In spite of the greater bulk of the precipitate it is best to employ a large excess of the standard solution of iron, for the highly basic arseniates of iron are less slimy and are far more easily washed than those which contain a larger proportion of arsenic. A good rule is to take one part by weight of metallic iron for every two parts of arsenious acid which the substance to be analyzed is supposed to contain.

The process is of course inapplicable when

the arsenical solution contains barium, calcium, strontium or any other metal whose arseniate is insoluble in ammonia-water.

Method B. The substance to be analyzed contains other non-volatile metals besides alkali metals. (V. Kobell's method). Mix the solution of arsenic acid with an excess of a standard solution of nitrate of iron, as in Method A, but instead of ammonia-water add an excess of carbonate of barium to throw down the basic arseniate of iron. If the arsenical solution be strongly acid it should be nearly neutralized with carbonate of sodium before adding the carbonate of barium. The liquid must be kept clear, however, until the moment when the barium carbonate is mixed with it. The mixture must not be heated but should be left to stand for several hours in the cold after the addition of the carbonate of barium. All the iron and all the arsenic will be thrown down in the form of basic arseniate of iron, while an equivalent proportion of the carbonate of barium dissolves. Wash the precipitate, which is of course mixed with the excess of the carbonate of barium, by decantation with cold water, collect it upon a filter, dry, ignite gently for some time (see Carbonate of Barium), and weigh. Dissolve the weighed precipitate in strong chlorhydric acid and determine the amount of barium by precipitation as Sulphate of Barium. From the amount of sulphate of barium found, calculate the equivalent quantity of carbonate of barium, add the weight of this carbonate to the weight of ferric oxide taken, and deduct the sum from the weight of the mixed precipitates of arseniate of iron and carbonate of barium; the difference will give the amount of arsenic acid contained in the substance analyzed.

The method cannot be applied directly in presence of metals precipitable by carbonate of barium in the cold. So, too, if sulphuric acid be present it must be removed by means of chloride of barium before the analysis can be proceeded with.

Properties of the Precipitate. The success of Method A depends materially on the state of aggregation of the precipitate. It must be a highly basic compound, neither slimy nor soluble in ammonia-water. The composition of the precipitate obtained in Berthier's process may be taken as varying from $2\text{Fe}_2\text{O}_3, \text{As}_2\text{O}_5$ to $16\text{Fe}_2\text{O}_3, \text{As}_2\text{O}_5$. The more basic it is the better. The $16\text{Fe}_2\text{O}_3$ salt is as insoluble in ammonia-water and as little slimy as ferric hydrate. It is to be observed that normal arseniate of iron ($2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}, 3\text{As}_2\text{O}_5 - 9\text{H}_2\text{O}$), as obtained by mixing a solution of ferric chloride with one of ordinary arseniate of sodium, is a white slimy precipitate soluble in ammonia-water and of no use to the analyst. Pfaff (*Handbuch analyt. Chem.*, Altona, 1824, I. 221 and 2. pp. 335, 344, 459, 476, 478, etc.), who thought highly of the principle now in question, as a means of separating iron from nickel and from manganese, describes the basic arseniate of iron as a

white pulverulent precipitate which falls immediately, even in presence of 25,000 parts of water. According to him, it is compact rather than gelatinous, and may be readily collected and washed; it is much more difficultly soluble than the benzoate or succinate of iron,—5 times less soluble than the last named salt. Pfaff obtained his precipitates by adding mono-arsenate of potassium to solutions of ferric salts. — It is worth inquiring whether the precipitate thus thrown down might not be weighed directly and then reduced with sulphur by H. Rose's method (see Arsenic Acid), in order to obtain the proportion of iron and of arsenic contained in it.

Arsenate of Lead.

Principle I. Fixity when heated to low redness.

Applications. Estimation of arsenious and arsenic acids in aqueous or nitric acid solutions free from chlorhydric acid and non-volatile substances, as well as ammonium salts and other reducing agents. Valuation of arsenious acid and metallic arsenic.

Method. Weigh a quantity of the solution to be examined in a tolerably large porcelain crucible, and, in case the solution contains no arsenious acid, mix with it directly a weighed quantity of pure, recently ignited, oxide of lead. Take 5 or 6 times as much oxide of lead as there is supposed to be arsenic acid in the substance, and stir it into the solution with a fine glass rod. Evaporate the mixture to dryness on a water bath, heat the residue to low redness and maintain it at that temperature for some time. Finally, weigh the residue and deduct the weight of the oxide of lead taken, in order to obtain the weight of the arsenic acid. The process affords excellent results provided the residue is not heated too strongly. — The oxide of lead is best prepared by igniting pure nitrate of lead.

In determining the value of any sample of metallic arsenic or arsenious acid, or in analyzing a solution of arsenious acid, dissolve the substance in nitric acid, or mix the solution with this acid, and evaporate the liquor to a small bulk before adding the oxide of lead. The dry residue must be ignited with special care in this case in order to avoid loss through decrepitation of the nitrate of lead. The crucible should be placed upon a sand bath at first in order to ensure a gradual elevation of the temperature, and should be kept covered. A similar remark applies of course to all cases in which nitric acid is present.

Principle II. Insolubility in water or acetic acid.

Applications. Separation of lead from many metals—among which may be mentioned Na, K, Li; Zn, Cd and Cu. (Pfaff).

Method. Mix the solution of arsenic acid, which must either be neutral or slightly acidulated with acetic acid, with an excess of a solution of acetate or nitrate of lead. Collect

the precipitate upon a filter, wash and dry it, ignite it gently apart from the filter, in a porcelain crucible, weigh and finally determine the amount of lead contained in the precipitate, as Sulphate of Lead. Another method of procedure is to dissolve the substance to be analyzed in nitric acid, to mix the solution with an excess of nitrate of lead, and to carefully evaporate the mixture to dryness in order to expel the free nitric acid. The dry residue, consisting of arseniate of lead, nitrate of lead, and nitrate of the metal previously combined with arsenious acid, is then washed with water and the arseniate of lead collected on a filter. The excess of lead must of course be removed from the filtrate before proceeding to determine the other metal or metals contained in it. Instead of evaporating the nitric acid solution of arsenic it may be carefully neutralized with an alkali and then mixed with acetate of lead. Unlike nitric acid, acetic acid dissolves scarcely any arseniate of lead, hence arsenic acid may be completely precipitated by adding acetate of lead to a solution of free arsenic acid without need of neutralizing or evaporating the liquid. Though inconvenient and almost obsolete, the process may still be employed in some cases. It is inapplicable in presence of chlorhydric acid or a chloride, for in that case insoluble or almost insoluble double compounds of chloride and arseniate of lead would be precipitated.

Properties. Pure arseniate of lead is a white powder, yellowish when hot, which softens at a low red heat. It fuses when heated strongly and is then apt to suffer slight decomposition, a small proportion of arsenic acid being lost in the form of arsenious acid and free oxygen. The substance actually weighed in the first of the two processes above described is not pure arseniate of lead; but a mixture of that substance with free oxide of lead. The product obtained by the second process is a variable mixture of tri- and di-arsenate of lead.

Arsenate of Magnesium and Ammonium.

Principle. Sparing solubility in ammoniated water, and fixity at 100°.

Applications. Estimation of arsenic acid in all solutions free from substances permanently precipitable by ammonia or by a magnesium salt. Separation of arsenic acid from all acids which form soluble magnesium salts. Separation of arsenic from arseniomolybdate of ammonium; from K, Na; Al, Zn, Cd; Mn, Ni, Co, Fe; Cu and Sb. Separation of arsenious from arsenic acid and of Mg from K and Na.

Method A. Absence of substances precipitable by ammonia or by magnesia. Add to the solution which contains arsenic acid ammoniated water in distinct excess, and stir into the liquid a mixture of sulphate of magnesium, chloride of ammonium and ammonia (see Sulphate of Magnesium) as long as a precipitate continues to fall. This "magnesia-mixture" consists of a solution of sulphate of magnesium charged

with so much chloride of ammonium that no magnesia can be precipitated from it by ammonia-water. Leave the liquid and precipitate at rest for 12 or 24 hours in the cold. Then collect the precipitate upon a weighed filter which has been dried at 105° – 110° . — The liquid should smell strongly of ammonia, after the addition of the magnesia-mixture, but should contain no more chloride of ammonium or other ammonium salt than is absolutely necessary to prevent the precipitation of hydrate of magnesium. The precipitate is in fact considerably more soluble in solutions of ammonium salts than in pure water. The liquid must never be heated, and time enough must be allowed for the precipitate to separate from it completely before filtering. Since the precipitate is by no means absolutely insoluble in ammoniated water, it must be washed with extreme care. In order to avoid using any more water than is absolutely necessary for the washing, transfer the precipitate from the beaker to the filter by means of portions of the filtrate, and afterwards wash it upon the filter with small quantities of a mixture of 1 part strong ammonia-water and 3 parts water until the washings give only a slight opalescence when acidulated with nitric acid and mixed with nitrate of silver. Dry at 105° – 110° and weigh.

The process yields satisfactory results, though on account of the solubility of the precipitate they are always somewhat lower than theory requires. According to Fresenius, this error may be partially corrected, as follows:—Measure the filtrate, without the washings, and for every 16 c. c. of the liquid add 1 m. g. to the weight of the precipitate. The wash water must not be measured since it cannot be regarded as a saturated solution of the double arseniate.

Instead of washing with ammoniated water, as above, H. Rose directs that the solution to be examined be concentrated to a small bulk, supersaturated with ammonia-water and mixed with one quarter its volume of strong alcohol before adding the magnesia mixture, and that the precipitate, after standing 48 hours in its liquor, be washed with a mixture of 4 vols. water, 1 vol. absolute alcohol, and a not too small quantity of ammonia-water.

In case any portion of the arsenic in the original solution is not already in the form of arsenic acid or an arseniate, the solution must be gently heated in a flask with nitric or chlorhydric acid, and small portions of chlorate of potassium thrown into the liquid until the latter emits a strong odor of chlorous acid. When all the arsenic acid has thus been oxidized, heat the liquid gently to drive off most of the chlorous acid, and proceed with the addition of ammonia-water and magnesia mixture as before.

Properties. The double arseniate is a white, somewhat transparent, crystalline precipitate,

of composition represented by the formula $2\text{MgO}, (\text{NH}_4)_2\text{O}, \text{As}_2\text{O}_5 + 12\text{H}_2\text{O}$. When heated to 105° – 110° it loses 11 equivalents of water, so that the formula of the compound actually weighed is $2\text{MgO}, (\text{NH}_4)_2\text{O}, \text{As}_2\text{O}_5 + \text{H}_2\text{O}$:—

2MgO	80	21.05
$(\text{NH}_4)_2\text{O}$	52	13.68
As_2O_5	230	60.63
H_2O	18	4.74
	<hr/> 380	<hr/> 100.00

The precipitate might be dried at 100° if only time enough were allowed. But at the temperature of a water bath, the precipitate retains 2 or 3 equivalents of water with considerable force.

On ignition the compound loses water and ammonia, and changes to arseniate of magnesium $2\text{MgO}, \text{As}_2\text{O}_5$. It is not impossible to obtain good results by igniting the precipitate and weighing the residuum as Levol (*Annales Chim. et Phys.*, (3) 17. 501), the inventor of the process, originally proposed. Wittstein (*Zeitsch. analyt. Chem.*, 1863, 2. 20), in reasserting the propriety of this course, directs that the crucible be placed at first on a sand bath and heated with a small spirit lamp until the odor of ammonia is no longer perceptible. Then remove the crucible from the bath and heat it over the free flame more and more strongly, almost to redness. H. Rose admits that by raising the temperature of the precipitate very gradually during several hours, from 100 to 400° , and then as gradually from dull to bright redness, all the water and ammonia may be expelled without losing any arsenic through the reducing action of the ammonia. But in case the dry precipitate is exposed directly to a high temperature, a very considerable portion of the arsenic is lost. According to his experiments, if the precipitate be gently heated for a short time and then brought to redness, no more than 96 per cent of the arsenic contained in the magnesium salt will ever be obtained, while results as low as 95 and 93 per cent are common. If the precipitate be exposed at once to a red heat, only about 88 per cent of the arsenic is left to be weighed. The precipitate might be ignited with bisulphate of ammonium and reduced to the condition of sulphate of magnesium (see Arsenic Acid) before weighing, were it not for the errors introduced by the action of the ammonium salt upon the material of the crucible. The double arseniate cannot be completely reduced, however, by igniting it with sulphur or with carbonate of ammonium, or in a current of hydrogen gas. (H. Rose, *Zeitsch. analyt. Chem.*, 1862, 1. pp. 418, 424).

Arseniate of magnesium and ammonium is much more soluble in pure water than in dilute ammonia-water or ammoniated spirit. It is more soluble in aqueous solutions of ammonium salts than in water, though the solvent power of these salts is diminished by the presence of

free ammonia. At the temperature of 15° according to Fresenius (*Zeitsch. analyt. Chem.*, 1864, 3, 207), 1 part of the salt (reckoned as dried at 100°) dissolves in 2656 parts of water; in 15038 parts of ammoniated water, made by mixing 1 part of ammonia-water, of 0.96 sp. gr., with 3 parts of water; in 1315 parts of a dilute and 844 parts of a strong solution of chloride of ammonium (containing respectively 70 and 7 parts of water to 1 part of chloride of ammonium); and in 2871 parts of a solution made by mixing 60 parts of water, 10 parts of ammonia-water, of 0.96 sp. gr., and 1 part of chloride of ammonium.

Method B. Separation of Arsenic Acid from Arsenious Acid. Mix the tolerably dilute solution of the two acids with a large quantity of chloride of ammonium and then precipitate the arsenic acid with magnesia mixture, as in A. The arsenious acid may be determined in the filtrate as Sulphide of Arsenic. If the original solution be too concentrated some arsenite of magnesium will go down with the double arseniate. To be sure of the purity of the latter it is well to dissolve it in chlorhydric acid, after weighing, and to test the solution with sulphuretted hydrogen. The immediate formation of a precipitate would indicate the presence of some arsenious acid.

Method C. Separation of Arsenic Acid from Cd, Zn, Al, Ur, Mn, Fe, Co, Ni and Cu. Dissolve the substance to be analyzed in chlorhydric or nitric acid, and in case the arsenic is not all in the condition of arsenic acid, bring it to that state by means of chlorate of potassium as in Method A. Mix the tolerably dilute solution with enough tartaric acid to prevent the formation of a precipitate by ammonia-water, and then with ammonia-water in excess. Finally add the mixture of sulphate of magnesium, chloride of ammonium and ammonia, and proceed as in Method A.

Since the precipitate, in this case, is liable to be contaminated with a difficultly soluble basic tartrate of magnesium, it is best, after washing once with the ammoniated water, to redissolve it in chlorhydric acid, to mix the solution with a very small quantity of tartaric acid, to supersaturate with ammonia and allow the whole to stand during at least 12 hours. The pure precipitate thus obtained may then be collected, washed, dried and weighed. The process is better suited for separating large than small quantities of arsenic acid from the metals in question, for if the proportion of arsenic be very small the amount of arseniate of magnesium and ammonium which is necessarily dissolved in the process of washing may exert a very considerable influence on the accuracy of the result.

With the exception of aluminum, the various metals may be thrown down as Sulphides from the original filtrate, by means of sulphhydrate of ammonium. To determine aluminum, evaporate the filtrate to dryness in a platinum

dish, roast the residue in a muffle to destroy sulphur and organic matter, fuse with carbonate of sodium, dissolve in chlorhydric acid and precipitate Hydrate of Aluminum.

Method D. Separation of Arsenic from Antimony. Proceed as in Method C. But immediately after adding the tartaric acid mix with the solution a large quantity of chloride of ammonium, before proceeding to saturate with ammonia-water. Any precipitate produced on the addition of the ammonia-water would go to show that the quantity of chloride of ammonium or of tartaric acid previously added was insufficient, and that a further portion of one or the other of these agents must be added before adding the magnesia mixture. — In case the substance to be analyzed is an alloy, or a mixture of sulphides, oxidize it in the manner described under Antimony. Finally determine the antimony in the filtrate as Sulphide of Antimony.

Method E. Determination of Arsenic Acid in a precipitate of Arseniomolybdate of Ammonium. Dissolve the precipitate upon the filter in ammonia-water, wash the paper thoroughly and add enough chlorhydric acid to the solution to neutralize a good part of the ammonia. Take care, however, to leave the solution clear and smelling strongly of ammonia. Finally add the magnesia mixture and proceed as in Method A.

Method F. To separate Magnesium from Potassium or Sodium, mix the solution with a quantity of chloride of ammonium, add ammonia-water in excess, and a solution of arseniate of ammonium as long as any precipitate falls. Allow the mixture to stand and treat the precipitate as in A. To determine the potassium or sodium, evaporate the filtrate from the double arseniate to dryness under a chimney and ignite the dry residue. The excess of arsenic acid goes off, together with the ammonium salts, while the alkali metals are left as chlorides, always contaminated, however, with a little chloride of magnesium. Magnesia may be separated more quickly from the alkalies in this way than by means of the double Phosphate of Magnesium and Ammonium, but the latter process is more accurate, and on the whole, more convenient than the one just described.

Arseniate of dinoxide of Mercury.

Principle. Insolubility in water.

Applications. Separation of arsenic acid from Na, K; Ba, Ca, Sr; Mg, Cd, Zn; Co, Ni, Pb and Cu.

Method. Same as that described under Phosphate of dinoxide of Mercury, excepting that the arsenic acid cannot be determined in the insoluble residue in the way that phosphoric acid is determined.

Arseniate of Potassium (or of Sodium).

Principle. Solubility in water.

Applications. (A). Separation of arsenic acid from Fe, Mn and Cu; less completely from Zn. (B). Separation of arsenic acid from many metals, including those of the alkaline earths.

Method A. Boil the finely powdered, unignited arseniate of iron, or other metal, for some time with a solution of a caustic alkali, or less advantageously with a solution of an alkaline carbonate. Dilute the liquor with water and filter it in order to separate the soluble arseniate of potassium or of sodium from the insoluble oxide or carbonate which remains undissolved. — Since oxide of zinc is soluble in caustic alkalis, arseniate of zinc must always be treated with a carbonated alkali. It is not easily decomposed in any event. (V. Kobell; H. Rose, *Zeitsch. analyt. Chem.*, 1862, 1, 425). It will not answer to simply precipitate the solution of a metallic arseniate with an excess of a solution of carbonate of potassium or of caustic potash, since more or less arsenic would almost always be retained by the precipitate. — The method is inapplicable for the analysis of native arseniate of iron, or of the artificial product after it has been ignited. Only a part of the arsenic can be removed from these substances by boiling alkali. (Berzelius).

Method B. Mix the powdered substance to be analyzed with 3 parts of dry carbonate of sodium, or better, with 3 parts of a mixture of equal equivalents of the carbonates of sodium and potassium, and melt the mixture at the blast lamp. The mixture of carbonate of sodium and carbonate of potassium melts more easily than either carbonate taken by itself. When the mixture has been thoroughly fused, all the arsenic acid will be found in the condition of arseniate of sodium, and the metals to be separated in the form of insoluble carbonates or oxides. Dissolve the fused mass in water, separate the soluble arseniate by filtration and estimate the arsenic acid as Arseniate of Magnesium and Ammonium.

The process is objectionable, inasmuch as no vessels can be found proper to be used for the fusion. There would be danger of destroying a platinum crucible through the combined action of an alkaline arseniate and reducing gases from the lamp; if a porcelain crucible is used its glazing will be dissolved by the melted alkali, and the solution of arseniate of sodium will thus become contaminated with aluminum and silicon. The risk of destroying a platinum crucible is lessened, and the fusibility of the flux increased, by mixing a quantity of nitrate of potassium with the carbonate; but the process cannot be commended unless the proportion of arsenic in the mixture to be analyzed is very small.

Arseniate of Tin (SnO_2).

Principle. Insolubility of the compound in water and dilute nitric acid, and fixity when ignited.

Applications. Estimation of tin and of arsenic in commercial stannate of sodium.

Method. Mix a weighed quantity of the stannate to be tested with a weighed quantity of arseniate of sodium, more than sufficient to precipitate the whole of the tin. Add an excess of nitric acid to the mixture and boil the liquid; collect the precipitate upon a filter, wash, dry, ignite and weigh. Determine also the arsenic acid in the filtrate by precipitating it as Arseniate of Magnesium and Ammonium. The amount of tin is found from the weight of the ignited arseniate of tin, and that of the arsenic by adding together the quantities of arsenic found in the arseniate of tin and the arseniate of magnesium and ammonium, and subtracting from this sum the quantity of arsenic added in the form of arseniate of sodium.

Properties. The composition of the washed precipitate may be represented by the formula $2\text{SnO}_2, \text{As}_2\text{O}_5 + 10\text{H}_2\text{O}$; and that of the ignited precipitate by the formula $2\text{SnO}_2, \text{As}_2\text{O}_5$. (E. Häffely, *Phil. Mag.*, (4.) 10, 291).

The same principle is involved in a method of estimating arsenic and tin in an alloy of the two metals, proposed by Levol (*Ann. Chim. et Phys.*, (3.) 16, 493). Levol has found that when an alloy of tin and arsenic, containing less than 5 per cent of arsenic is boiled with nitric acid, the whole of the arsenic will remain in insoluble combination with the oxide of tin, in the form of basic arseniate of tin. Even when the alloy contains 8 per cent of arsenic, little or no arsenic will remain dissolved in the excess of nitric acid, but when the proportion of arsenic exceeds 8 per cent some of it always goes into solution. The process of analysis is as follows:—Treat the finely laminated alloy with tolerably strong nitric acid, first in the cold, in order that stannous oxide may be formed, and afterwards at the temperature of boiling to convert the stannous into stannic oxide. Collect the arseniate of tin upon a filter, dry and weigh it and finally heat it in a current of hydrogen to determine the proportion of Arsenic. In case the filtrate also contains arsenic, estimate the quantity by precipitating as Arseniate of Magnesium and Ammonium or in some other appropriate way.

Levol has applied this method to the estimation of arsenic in metallic copper. He dissolves the metal in nitric acid, mixes the solution with a solution of stannous nitrate, prepared in the cold, and boils the mixture. Stannic arseniate is thrown down from the hot liquor, and the proportion of arsenic contained in it is estimated in the manner already described.

Arseniate of Uranium.

Principle. Insolubility in water and acetic acid.

Applications. Estimation of arsenic in arsenic and arsenious acids and in arseniates and

arsenites of the alkali-metals. (Method A). Estimation of arsenic as in A, and also in presence of Ba, Sr, Ca, Mg and Zn; but not in presence of metals, such as Cu, which are precipitated by ferrocyanide of potassium (Method B).

Method A. Gravimetric. Boil the solution of arsenic acid with an excess of potash lye, supersaturate the mixture with acetic acid, and add to the clear solution an excess of acetate of uranium. Wash the precipitate with a very dilute solution of chloride of ammonium and finally remove the chloride of ammonium by washing with a mixture of 1 volume of alcohol and 8 or 9 volumes of water. Dry the precipitate at a gentle heat upon a water bath and ignite it moderately in a porcelain crucible for a long time. The crucible must not be heated to redness.

Precautions. The solution to be analyzed must be free from ammonium salts; if ammonium salts were present ammonia would be thrown down in combination with the precipitate and would reduce some of the arsenic acid when the precipitate came to be heated. No metals of the alkaline earths or other substances precipitable by arsenic acid should be present. The solution must be perfectly clear after the addition of acetic acid. Precipitated arseniate of uranium is apt to be so finely divided that it would pass through the pores of the filter if simply washed with water. This difficulty is avoided by washing with chloride of ammonium instead of water. As a rule the method is less convenient than that depending on the insolubility of Arseniate of Magnesium and Ammonium. (Werther, *Journ. Prakt. Chem.*, 43. 346).

Properties. The precipitate first thrown down, of composition $2\text{U}_2\text{O}_3 \cdot \text{H}_2\text{O}$, As_2O_5 , is insoluble in water, acetic acid and saline solutions, particularly in a solution of chloride of ammonium. The composition of the residue left after ignition may be represented by the formula $2\text{U}_2\text{O}_3$, As_2O_5 . The proportion of arsenic can be calculated from it directly.

Method B. Volumetric. Prepare a solution of nitrate of sesquioxide of uranium of such strength that a litre shall contain about 20 grammes of the sesquioxide. This solution should contain as little free acid as possible. To standardize the liquor weigh out a quantity of pure arseniate of sodium, dissolve it in water, supersaturate the solution with ammonia water, and finally make the liquor distinctly acid with acetic acid. Slowly pour the uranium solution from a burette into the acidulated solution of arsenic acid, with constant stirring, until a drop of the liquid placed upon a porcelain plate gives a reddish brown coloration when tested with ferrocyanide of potassium. Note the quantity of uranium solution used; mark the height of the liquid in the beaker by means of a strip of gummed paper; empty and wash the beaker and fill it to the mark with

water charged with about as much ammonia and acetic acid as were previously added to the arseniate of sodium. Pour uranium solution from the burette into this acidulated water until a drop of the solution gives the red brown reaction with ferrocyanide of potassium. — A certain excess of the uranium solution has always to be used in order to obtain the reaction with ferrocyanide of potassium, and the purpose of the second titration is to determine the amount of this excess for the particular degree of dilution involved in the given case. The number of c. c. of uranium solution employed in the second titration must be subtracted from the quantity first used, in order to obtain the true value of the solution with reference to arsenic acid. To be sure of the final reaction, spread out a drop of the liquor upon porcelain and place a drop of the ferrocyanide in the centre of the spot; if the titration be finished a distinct reddish brown line will form where the two liquids meet. — Instead of arseniate of sodium pure arsenious acid may be used for standardizing the liquid; after having been weighed it must be converted into arsenic acid by boiling with fuming nitric acid.

In an actual analysis, the substance, after having been brought to the condition of arsenio acid, is treated with ammonia water and acetic acid, and the clear solution titrated with the uranium solution, as above described. The second titration, to determine the correction for dilution, must be made in every analysis precisely as when the test liquor is standardized. In practised hands the process is said to yield good results. A solution of nitrate of uranium is preferable to the acetate, since the latter gradually decomposes when exposed to light. (Bœdeker, *Annal. Chem. und Pharm.*, 117. 195).

Arsenic. [Compare Arsenious Acid].

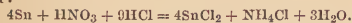
Arsenic is weighed either as metallic arsenic, as arseniate of iron (Fe_2O_3), arseniate of lead, arseniate of uranium, arseniate of magnesium and ammonium, or as tersulphide of arsenic. It may be estimated by loss either as As, as AsCl_3 , or as As_2S_3 , by titration with oxidizing agents, as will be explained under arsenious acid, and by indirect methods to be explained below. (See also the finding list in Appendix).

Principle 1. Sparing solubility of the metal in chlorhydric acid.

Applications. Separation of arsenic from tin.

Method. Heat the granulated or laminated alloy gently in a mixture of 1 equivalent of nitric acid and 9 equivalents of chlorhydric acid. The tin alone will dissolve, while metallic arsenic is left in the form of a powder, which may be collected upon a tared filter, washed, first with cold recently boiled water, then with alcohol, and dried at 100° . The acid must not be used in much larger proportion than 1 equivalent nitric acid and 9 equivalents chlorhydric acid to 8 equivalents of the arseniated tin.

When the acids are used in these proportions the solution of the tin is unaccompanied by the evolution of gas, the chlorides of tin and of ammonium being the sole products besides water.



(Gay-Lussac, *Annales Chimie et Phys.*, [3.] 23. 228).

For the separation of arsenic from an alloy of tin, antimony and arsenic see under Antimony, Principle I., No. 3.

Principle II. Volatility.

Applications. Separation of arsenic from antimony and from tin.

Method A. To separate arsenic from antimony weigh out some of the finely divided alloy in a bulb tube, mix with it 2 parts of carbonate of sodium and 2 parts of cyanide of potassium, and connect the tube with a source of dry carbonic acid. After all the air has been expelled, heat the tube gently for a while, afterwards gradually increase the heat to intense ignition, and continue to heat until all the arsenic has been volatilized and driven from the tube. After removing the lamp, continue the current of carbonic acid until the tube has become cold, then lixivate the contents of the tube, first with a mixture of equal parts of strong alcohol and water and afterwards with water. Finally, dry and weigh the residual antimony. The quantity of arsenic is inferred from the loss. The method is said to yield only approximate results.

In case it is desired to dispense with the carbonate of sodium and cyanide of potassium and to fuse the alloy by itself in the current of carbonic acid, special care must be exercised in heating the alloy or much antimony will be driven off with the arsenic.

2. To separate arsenic from tin. Oxidize the alloy with nitric acid in a beaker, wash the product into a porcelain crucible with a solution of carbonate of sodium, evaporate to dryness on a water bath, mix the dry residue with equal parts of carbonate of sodium and cyanide of potassium, and melt the mixture. All the arsenic is driven off in the form of vapor while the tin remains, partly in the form of metal and partly as oxide, and as stannate of sodium. The tin is estimated as Oxide of Tin and the arsenic by the difference.

In case the substance to be analyzed is arseniate of tin, weigh out some of it in a glass boat, introduce the boat into a wide glass tube, pass a current of hydrogen through the tube and heat the tube to dull redness. Metallic arsenic sublimates and is deposited as a coating upon the colder part of the tube. Its weight is determined by cutting off that part of the tube and weighing it first with the arsenic and again after the arsenic has been dissolved. In order to retain any arsenic which might go forward as arseniuretted hydrogen, it is well to lead the escaping gases through a short column of weighed hot metallic copper. Or the whole

of the volatilized arsenic may thus be made to combine with copper in one operation.

Since the tin always retains some arsenic, it must be dissolved in chlorhydric acid, and the mixture of hydrogen and arseniuretted hydrogen evolved, after having been freed from chlorhydric acid by washing with soda lye, must be made to pass into a solution of nitrate of silver. The arsenic in the gas is thus converted into arsenious acid while metallic silver is thrown down. In case any solid arseniuretted hydrogen (or insoluble alloy of arsenic) is left undissolved by the chlorhydric acid, it must be dissolved in a few drops of nitric acid. The excess of silver is then thrown down as Chloride of Silver; the filtered arsenious acid is mixed with the nitric acid solution of the solid residue, and the arsenic precipitated as Sulphide of Arsenic. — As a substitute for this method of procedure Berzelius recommends that the arseniuretted hydrogen from the solution of the tin, be decomposed by passing it through a weighed quantity of red-hot copper, and that the solid residue be neglected.

3. The old method of separating arsenic from certain alloys by roasting the mixture in a current of air until the odor of garlic was no longer perceptible, or heating with admixture of charcoal, in case the arsenic were present as arsenic acid, gave only approximative results. For that matter, metals like nickel, cobalt and iron, always retain a certain portion of the arsenic. (Pfaff, *Handbuch analyt. Chem.*, 1825, 2. 426).

Principle III. Oxidation by chlorine in alkaline solutions (Method A), by aqua regia, by a mixture of Chlorate of Potassium and nitric or chlorhydric acid (Method B), or by Nitrate of Potassium.

Applications. Separation of As from Fe, Co, Ni and Cu (Method A); from Sb (Method B); from Ca, Ba, Sr; Mg, Zn, Cd, Mn, Fe, Co, Ni; Ag, Pb, Hg, Cu, Bi (Method C).

Method A. Oxidation by Chlorine. Same as the methods described under Antimony. A solution of arseniate of potassium is produced.

Method B. Oxidation by Aqua regia or by a mixture of Chlorate of Potassium and Nitric or Chlorhydric Acid. Same as the methods described under Antimony. In order to avoid the volatilization of tetrachloride of arsenic, care must be taken never to evaporate a solution which contains arsenious acid and chlorhydric acid unless free chlorine or chlorous or nitric acid be also present.

Method C. Oxidation by Nitrate of Potassium. Fuse the alloy with a mixture of 3 parts of carbonate of sodium and 3 parts of nitrate of potassium. Boil the fused mass with water, separate the soluble alkaline arseniates from the insoluble oxides and carbonates, by filtration and washing with hot water, and determine the arsenic as Arseniate of Magnesium and Ammonium. — In case the proportion of

arsenic in the alloy is not large, the fusion may be effected in a platinum crucible, in the bottom of which a layer of carbonate of potassium has been placed before introducing the mixture. When a porcelain crucible is used, part of it is dissolved by the melted alkali and the fused mass is consequently contaminated with silicon and aluminum. (Wöhler, *Pogg. Ann.*, 25. 302).

In order to avoid loss of arsenic by volatilization, alloys rich in arsenic had better be oxidized with nitric acid in the first place and the dry residue subsequently fused with 3 parts of carbonate of sodium and 1 part of nitrate of potassium.

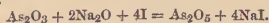
Arsenious Acid. [Compare Arsenic Acid].

Principle. Oxidation by Iodine (A), by Chlorine (B), by Bichromate (C), Permanganate (D), Nitrate (E), or Chlorate (F), of Potassium; by aqua regia or by Salts of Gold (G).

Applications. Methods A B C and G may be employed for determining arsenious acid in arsenites and in the commercial acid; for separating arsenious from arsenic acid and for determining arsenic in boiled chlorhydric acid solutions of sulphide of arsenic. Method A is well suited for determining the amount of arsenious acid in commercial realgar and orpiment. It may be used for estimating iodine, and also for standardizing iodine solutions,—as will be explained under Iodine,—by which to estimate Chlorine, Bromine, Ozone; Hypochlorous, Chloric, Chromic, Sulphurous and Sulphydric Acids; the higher Oxides of Manganese, Cobalt and Nickel; in short, all oxides which evolve chlorine when heated with chlorhydric acid; and tin in Stannous salts.

Method B is largely used for estimating the value of bleaching salts. — Method E serves to separate arsenic from Ca, Ba, Sr; Mg, Cd, Zn, Mn, Fe, Co, Ni; Ag, Pb, Hg, Cu and Bi. Method F may be used for determining nitric acid, as well as for converting arsenious into arsenic acid in the ordinary course of analysis.

Method A. Oxidation by Iodine in Alkaline Solutions.



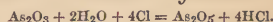
Weigh out as much of the substance to be analyzed as will contain about 0.1 grm. of arsenious acid, and dissolve it by boiling with 20 c. c. of a saturated aqueous solution of pure bicarbonate of sodium. Stir some starch paste into the solution, and afterwards pour in a standard solution of Iodine from a burette, until the whole liquid just becomes blue. If the substance to be analyzed is an acid solution it must be neutralized with pure carbonate of sodium, and if alkaline with pure chlorhydric acid, before mixing it with the bicarbonate. Results accurate.

To determine arsenious acid when mixed with sulphide of arsenic, boil the mixture with carbonate of sodium, dilute with water and

acidulate with acetic acid; filter, to remove the sulphide of arsenic which is thrown down, supersaturate the filtrate with bicarbonate of sodium, and proceed with the titration. The substance to be analyzed and the carbonate of sodium must be wholly free from sulphurous acid, hyposulphites and other substances capable of acting upon iodine. (F. Mohr, *Titrir-methode*, 1855, p. 295).

To separate arsenious from arsenic acid determine the amount of arsenious acid in one portion of the substance, by titration with iodine as above, then oxidize the arsenious acid in another portion by means of nitric acid and chlorate of potassium (Method F), or by chlorine in alkaline solution, and determine the total amount of arsenic as Arseniate of Magnesium and Ammonium. Calculate the amount of arsenic acid from the difference.

Method B. Oxidation by Chlorine.



1. *By chlorine acting in an acid solution.*

The old method of chlorimetry devised by Gay-Lussac (*Annal. der Chem. und Pharm.*, 18. 18), which was formerly much used, depends upon the action of chlorine upon arsenious acid in chlorhydric acid solution.

A weighed quantity of pure arsenious acid was dissolved in hot concentrated chlorhydric acid, and the solution colored with two or three drops of a solution of indigo in sulphuric acid. A weighed quantity of the bleaching powder to be tested was mixed with water to a definite volume, and portions of the milky liquor were poured from a burette into the solution of arsenious acid, until the blue color of the indigo disappeared. — The process is distinctly inferior in several respects to that in which the chlorinated liquor is made to act upon arsenious acid in alkaline solution. Notably, because the oxidizing power of chlorine is less decided in presence of an acid than in that of an alkali, and because some chlorine is always set free by the action of the acid and lost, at the moment when the bleaching powder solution comes in contact with the arsenical liquor. As an indicator, moreover, indigo is inferior to the mixture of iodide of potassium and starch employed in the alkaline process. In practice, the color of the indigo does not disappear all at once; it is destroyed gradually by the local action of chlorine, wherever that agent happens to be in excess in any part of the liquor, and is not reproduced by the action of unoxidized arsenious acid in another part. Hence it is often necessary to add a fresh drop of indigo towards the close of the titration in order to be sure of the point of saturation.

2. *By Chlorine acting in an alkaline solution.* [Compare the description of this method under Antimony].

As applied to the estimation of the value of bleaching powder (after Penot, *Bulletin de la Société Industrielle de Mulhouse*, 1852, and *Dingler's polytech. Journ.*, 1853, 127. 134), the

process may be conducted as follows:—Heat a mixture of 4.4341 grms. of pure arsenious acid and about 13 grms. of crystallized carbonate of sodium in 600 or 700 c. c. of water, until the arsenic has all dissolved. Cool the solution and afterwards dilute it to 1 litre. Each cubic centimetre of this solution contains 0.004434 gm. of As_2O_3 , corresponding to 1 c. c. of chlorine gas at 0° and 76 m. m. pressure.

Weigh out 10 grammes of the bleaching powder, rub it in a tolerably large mortar with a little water, to a smooth paste; gradually add more water, until the mass becomes fluid, and transfer the liquid little by little to a litre flask, taking care to rub the residues in the mortar with fresh quantities of water as long as any heavy lumps remain. Fill the flask with water to the litre mark, and mix the milky liquor thoroughly by shaking. Each c. c. of this solution will contain 0.01 gm. of the bleaching powder. — By means of a marked pipette, measure into a beaker 50 c. c. of the freshly shaken, milky solution of bleaching powder, and pour into it the arsenical solution from a 50 c. c. burette, until a drop of liquid taken from the beaker fails to produce a blue spot on iodo-starch paper. The contents of the beaker must be stirred continually during the addition of the arsenical liquid, and the latter must be poured in slowly,—at last drop by drop. It is easy to hit the point of saturation exactly, since the successive blue spots produced on the paper gradually become fainter and fainter, and warn the operator to proceed more and more slowly. — If the operations were reversed, and the solution of bleaching powder were poured into the arsenical solution until a drop of the mixture gave a blue spot, this premonition would be lost. Another objection to this inverse method of working would be found in the tendency of bleaching powder solutions to froth,—whereby it becomes difficult to read the indications of the burette,—and to soil the burette. But, as Penot has suggested, it is sometimes well to resort to the inverse method for the sake of controlling the accuracy of an experiment made in the ordinary way.

The number of half cubic centimetres used of the standard arsenious solution, indicates directly the number of French chlorimetrical degrees; i. e., the number of litres of chlorine gas, at 0° and 76 m. m. pressure contained in 1 kilogramme of the bleaching powder. For example: In case 35 c. c. of the arsenical solution were consumed, then the quantity of bleaching powder used would contain 35 c. c. of chlorine gas. But the portion of bleaching powder solution taken (50 c. c.) contained 0.5 gm. of the powder; hence 0.5 gm. of the bleaching powder contains 35 c. c. of chlorine. and 1000 grms. contain 70,000 c. c. = 70 litres. It is for the sake of these degrees that the standard solution of arsenious acid is made

of the given strength, as will appear from the following proportion:—

$$\begin{array}{rcl} \text{Wt. of 4 Atoms} & \text{Wt. of 1 Molec.} & \text{Wt. of 1 litre} \\ \text{of chlorine} & \text{of } As_2O_3 & \text{of Cl gas} \\ 142 & 198 & 3.18002 \end{array} = x$$

where $x = 4.4341$, or the quantity of arsenious acid that 1 litre of chlorine can convert into arsenic acid. — To obtain directly the chlorimetrical degrees employed in England and America, take 6.9718 grms. of arsenious acid for the standard solution instead of the quantity stated above, and dissolve to the volume of 1 litre. 1 c. c. of this liquid will be equivalent to 1 c. c. = 0.005 gm. of chlorine. The number of c. c. used will consequently indicate the per cent of chlorine, if 0.5 gm. (50 c. c.) of the bleaching powder be taken as before. — The method of converting French or “Gay-Lussac” degrees into per cents, will appear from the following examples:—Bleaching powder of 90° Gay-Lussac contains $90 \times 3.18002 = 286.2018$ grms. chlorine in 1000 grms., or 28.62 in 100. A sample containing 34.2 per cent chlorine would mark 107.5°, for if 100 grms. contain 34.2 grms. Cl, and 1000 grms. contain 342 gm. Cl, then $342 \div 3.18002 = 107.5$, i. e., 1000 grms. of the powder contain 107.5 litres of chlorine.

For a complete table of per cents corresponding to Gay-Lussac degrees, see L. Müller in *Dingler's polytech. Journ.*, 1853, **129**, 286.

To prepare the iodo-starch paper, grind up 3 grms. of white starch in 250 c. c. of water, boil the mixture, with constant stirring; add an aqueous solution of 1 gm. iodide of potassium and 1 gm. crystallized carbonate of sodium, dilute with water to 500 c. c.; soak strips of printing paper in the liquor, dry them quickly in pure air, and keep in tightly stoppered bottles for use.

The process is accurate and of easy application. The standard arsenical solution undergoes no change on keeping, provided the arsenious acid and the carbonate of sodium used for preparing it are both absolutely free from easily oxidizable matters; such as sulphides or sulphites. (Mohr, *Titrir-methode*, 2d Edition, 1. 290). When prepared from ordinary materials the alkaline solution of arsenious acid is liable to oxidize slowly in the air. But even in this case, all difficulty may be avoided by keeping the solution in a number of small glass-stoppered bottles, each completely filled with the liquid, and using a fresh bottle for every new series of experiments. (Fresenius).

According to Fresenius (*System Quant. Anal.*, Art. Chlorimetry), much more constant and accurate results are obtained by operating with the turbid solution, or rather emulsion, of bleaching powder above described, than can be got by filtering the liquor, or allowing it to settle, and operating upon the clear portion. The emulsion should always be shaken just before any portion of it is taken for analysis.

Attempts of Mohr (*Titrirmethode*, 1855, p. 287) to do away with the iodo-starch paper, by mixing a definite quantity of the standard arsenical solution with starch paste and iodide of potassium, and pouring bleaching powder solution into the mixture, from a burette, resulted in failure. So much of the starch was destroyed by the hypochlorite, wherever it happened to be in excess for a moment, that no useful results could be obtained.

Another modification of the process, however, suggested by Mohr (*Ibid.*, pp. 323, 290), gives accurate results. In this case a definite quantity of the bleaching powder solution is measured into a beaker, and rapidly titrated with a standard solution of arsenious acid,—prepared by dissolving 4.9 grms. of pure arsenious acid in an aqueous solution of 20–25 grms. of pure crystallized carbonate of sodium, with the aid of heat, and subsequently diluting to 1 litre,—until a drop of the mixture ceases to turn iodo-starch paper blue. The excess of arsenious acid which has been used is then accurately determined by adding some starch paste to the mixture in the beaker, and pouring in a standard solution of Iodine, until the starch becomes blue. The amount of arsenious acid which corresponds to the quantity of iodine solution used, is then subtracted from the amount of arsenious acid which was poured into the beaker, in order to obtain the precise amount consumed by the chlorine of the bleaching powder.

Other applications. Both processes are of course applicable to the valuation of “chloride of soda,” and other hypochlorites, as well as to that of bleaching powder. They may be used also for analyzing compounds of the other chlor-oxygen acids; for determining chlorine, and for analyzing many oxygen acids and peroxides which evolve chlorine when heated with chlorhydric acid.

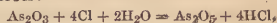
An aqueous solution of chlorine may be mixed immediately with a measured quantity of the standard solution of arsenious acid; while gaseous chlorine may either be received directly in a measured quantity of the standard arsenic solution, or better, in an unmeasured excess of bicarbonate of sodium solution. In the first case, some starch solution is added to the mixture after the chlorine has been absorbed, and the excess of arsenious acid is estimated by means of a standard solution of Iodine. In the second case, the standard solution of arsenious acid is poured into the alkaline mixture, until a drop of the latter placed upon iodo-starch paper ceases to color it; some drops of starch solution are then added to the liquor, and the slight excess of arsenious acid which has been added is determined by means of the standard iodine. — In neither case should any starch be added to the solution, until after the chlorine has all been absorbed and combined by the action of the arsenious acid.

In case the value of binoxide of manganese, chlorate of potassium, or bichromate of potassium is to be estimated by this process, or any analogous compound or peroxide is to be analyzed, boil the substance with an excess of concentrated chlorhydric acid, absorb the chlorine in arsenite or bicarbonate of sodium, and estimate it as above. Compare the next Method (by nascent chlorine).

3. *By nascent chlorine.* See Chromic Acid. (Reduction of by chlorhydric acid). If a weighed quantity of a chromate, such as bichromate of potassium, for example, is boiled with concentrated chlorhydric acid, chromic acid is reduced and chlorine set free in equivalent proportion, in accordance with the equation:—



The precise amount of Chlorine set free may readily be determined in a variety of ways. (Compare the last paragraph of the preceding Method). One method is to conduct the gas into a solution of iodide of potassium and to estimate the iodine, which the chlorine liberates, by means of a standard solution of hyposulphite of sodium, or by sulphurous acid. (See Iodine). But if arsenious acid, or an arsenite be added to the mixture of bichromate of potassium and chlorhydric acid before this mixture is heated, a definite quantity of the chlorine will be consumed in converting arsenious acid into arsenic acid, in accordance with the equation:—



and just so much less Cl will pass forward to be absorbed by the solution of iodide of potassium.

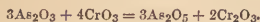
By operating with weighed quantities of bichromate of potassium it is easy to determine in one sample how much chlorine is set free in the absence of arsenious acid, and in a second sample how much less chlorine is given off after the addition of a weighed quantity of arsenious acid. The quantity of arsenious acid must of course always be less than sufficient to consume all the chlorine which the quantity of bichromate taken can evolve. Besides arsenious acid, the process may be applied for determining ferrous oxide, either by itself or in presence of ferric oxide, and other substances which are easily and completely oxidized by nascent chlorine, as will appear under the several headings. (Bunsen, *Annal. der Chem. und Pharm.*, 1853, 86. 290). — It may here be remarked that the process, though rapid and accurate, requires care and a sensitive balance. If no arsenious acid were present, 0.2 grm. of a chromate containing 50 per cent of chromic acid would be enough for an analysis. If more were taken, an inconveniently large quantity of hyposulphite of sodium would have to be used. A gramme of bichromate of potassium would require 500 c. c. of hyposulphite of the ordinary strength. (Hinman). The cost of iodide of potassium is an

objection, moreover, when any considerable number of analyses are to be made.

Method C. Oxidation by Bichromate of Potassium.

1. *Volumetric.* Method and precautions described under Antimonious Acid. See also biChromate of Potassium (Kessler, *loc. cit.*). See also the preceding paragraph,—oxidation of As_2O_3 by nascent chlorine.

2. *Gravimetric.* Mix the substance to be examined with a weighed quantity of pure, dry bichromate of potassium, place it in a suitable vessel and add strong sulphuric acid. A quantity of chromic acid will be reduced by the arsenious acid, in accordance with the equation:—



Determine how much chromic acid is left, by means of oxalic acid (see Chromic Acid, reduction of by oxalic acid), and calculate how much arsenious acid must have been present to reduce the remainder of the chromic acid taken. (Vohl, *Annalen Chem. und Pharm.*, 94. 219).

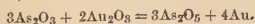
Method D. Oxidation by Permanganate of Potassium. The process is attended with difficulties which have not yet been fully overcome. (Kessler, *Poggendorff's Annalen*, 118. 17; Lenssen, *Journ. prakt. Chemie*, 78. 197).

Method E. Oxidation by Nitrate of Potassium. Same Method as that described under Arsenic, with the exception that a smaller proportion of nitrate of potassium is needed. A mixture of 3 parts carbonate of sodium and 1 part nitrate of potassium, is sufficient for the fusion of an arsenite. The fusion may be effected in a platinum crucible.

Method F. Oxidation by Aqua regia, or by Chlorate of Potassium. Method described under Antimony and Arsenic.

According to Stein, this principle may be used for estimating nitric acid. To this end, mix the nitrate to be analyzed with 3 parts of arsenious acid, dissolve the mixture in concentrated chlorhydric acid, and evaporate to dryness. Take up the residue with water, and determine the arsenic acid by precipitating it as Arseniate of Magnesium and Ammonium.

Method G. Oxidation by Salts of Gold. Mix the solution which contains arsenious acid with an excess of a solution of chloraurate of sodium, or chloraurate of ammonium, and allow the mixture to stand in a covered beaker for several days at the ordinary temperature. Collect and weigh the precipitated Gold, and from its weight calculate that of the arsenic in the solution, in accordance with the reaction:—



In case the original solution is very dilute, it had better be left to stand in a place slightly warmer than the ordinary air. It is well to keep the filtrate from the metallic gold, and to collect any further portion of gold which may be deposited from it. Even from the original solution the gold is deposited very slowly upon

the walls of the beaker. The beaker should be new and smooth, for it is difficult to wash out the precipitated gold from a beaker which has become roughened by use. The solution must be free from nitric acid and other oxidizing agents, and must be protected from dust also. A considerable excess of chlorhydric acid, however, appears to do no harm. In case the substance to be analyzed is solid, it should be dissolved in chlorhydric acid.

Though inferior to Method A, the gold process is reputed to yield accurate results, and to be free from the sources of error which have led to the abandonment of the process as applied to the determination of Antimonious Acid. The inventor of the process, H. Rose, remarks that its results would probably be less accurate in case too large a proportion of chloride of sodium, or of chloride of ammonium, were mixed with the chloride of gold in preparing the chloraurate.

In order to be fit for use as a reagent, arsenious acid should volatilize without residue, and should yield no brownish coloration when 10 or 12 grms. of it are dissolved in a solution of pure carbonate of sodium, and tested with a drop or two of a solution of acetate of lead. The brown color thus produced is due to the presence of sulphide of arsenic; and in case a residue is left on heating, which turns black when ignited in a current of hydrogen, the presence of antimony is indicated.

The solid cakes of arsenious acid to be obtained of importers of pure chemicals, are generally quite pure.

Arseniomolybdate of Ammonium.

Principle. Insolubility in water, and in acid and saline solutions.

Applications. Separation of arsenic acid from Na, K, NH_4 , Li; Ba, Sr, Ca, Mg; Al, Cr, Fe, Mn, Co, Ni, Zn, Cd, Pb, Bi, Ag, Hg and Cu. Estimation of arsenic acid in solutions free from phosphoric and silicic acids, and from substances capable of decomposing molybdic acid.

Method. Prepare a solution of molybdate of ammonium by heating 10 grms. of that salt with 40 c. c. of ammonia water of 0.96 specific gravity, pour the solution into a mixture of 120 c. c. strong nitric acid, and 40 c. c. of water, and let the whole digest for 8 or 10 hours, at 40°. Allow the mixture to settle, and decant the clear liquid.

Mix the solution which contains the arsenic acid with a large proportion of the aforesaid solution of molybdate of ammonium, add enough nitric or chlorhydric acid to redissolve the precipitate of molybdic acid which forms at first, and boil the solution for a long time. If molybdic acid has been added in excess, arseniomolybdate of ammonium will be thrown down in the form of a yellow precipitate. The subsequent operations are similar to those de-

scribed under Phosphomolybdate of Ammonium. Since it is not easy to separate molybdic acid from the filtrate, a new portion of the original substance had better be taken for the determination of the metals with which the arsenic acid was originally combined.

Properties. Arseniomolybdate of ammonium is well nigh insoluble in water, saline solutions and acids, especially nitric acid, provided an excess of molybdate of ammonium be present, together with a moderate excess of nitric or chlorhydric acid. The composition of a sample of the precipitate analyzed by Seligsohn (*Journ. prakt. Chem.*, **67**, 481), was molybdic acid 87.67 per cent; arsenic acid 6.31 per cent; ammonia 4.26 per cent, and water 1.77 per cent. Since its composition is variable, the precipitate is never weighed directly. It is dissolved in ammonia-water, and Arseniate of Magnesium and Ammonium is precipitated from the ammoniacal solution.

Atropin. See Iodo-Mercurate of Atropin.

Barium is usually determined as Sulphate or Carbonate, but sometimes as Fluosilicate of Barium. For its alkalimetric estimation, see Oxide and Carbonate of Barium. See also the finding list for Barium, in the Appendix.

Baryta. See Hydrate of Barium.

Basic Benzoate of Iron (Ferrie benzoate).

Principle. Insolubility in water.

Applications. Separation of Fe from Mn, Ni and Zn.

Method. Same as that described under Succinate of Iron.

When benzoic acid, or rather, when the alkaline benzoates can be obtained at less cost than succinic acid and the succinates, it is better to precipitate iron as a benzoate (Hisinger & Berzelius). Basic benzoate of iron is indeed slightly less soluble than the corresponding succinate, but this advantage is balanced by the fact that the precipitated benzoate is more voluminous than the succinate. Moreover, it contains much more carbon than the latter; but this difficulty can be overcome, as with the succinate, by leaching the precipitate with dilute ammonia-water, until most of the benzoic acid is removed.

Bismuth may be determined as metallic Bismuth, Carbonate, Chromate, Oxide or Sulphide. For a list of methods for separating it from the other metals, see Appendix.

Principle I. Insolubility of the metal in dilute nitric or acetic acids in presence of metallic lead or zinc.

Applications. Separation of bismuth from certain other metals,—notably from lead.

Method A. Precipitate the bismuth by metallic zinc, from a dilute nitric acid solution. (*Pfaff, Handbuch analyt. Chem.*, 1825, **2**, 401).

Method B. Dissolve the alloy in nitric acid, dilute the solution with a large quantity of water, and place in it a strip of pure metallic lead. The bismuth will be precipitated rapidly and completely, in the form of a black powder. As soon as the precipitation is finished, decant the clear acidulated liquor, wash off adhering particles of bismuth from the strip of lead, and wash the precipitate rapidly by decantation, first with water, and then with alcohol. Collect the precipitate upon a small weighed filter, dry and weigh. (*Patera, Zeitsch. analyt. Chem.*, 1866, **5**, 226).

Method C. After having brought the mixture of bismuth and lead into solution, throw down both the metals as carbonates, by means of carbonate of ammonium, dissolve the precipitate in acetic acid, and place in the solution a weighed piece of pure sheet lead. Cover the beaker, and leave it at rest for several hours, taking care that no part of the lead projects above the surface of the liquid. When all the bismuth has been precipitated, wash the strip of lead, and dry and weigh it. The difference between the first and last weight of the lead indicates how much of this metal has been added to the solution. Collect the precipitated bismuth upon a filter, and wash it with water which has been boiled to expel air, and afterwards cooled. Dissolve in nitric acid, and precipitate Carbonate of Bismuth; or evaporate the nitric acid solution to dryness, and ignite the dry residue to obtain Oxide of Bismuth. Lead may be determined in the filtrate by precipitating it as Carbonate of Lead. (*Ullgren, Berzelius's Jahresbericht*, **21**, 148).

Principle II. Fixity, when heated.

Applications. Estimation of bismuth in the oxide, sulphide, oxychloride and salts of this metal.

Method. Fuse the compound to be analyzed in a capacious porcelain crucible, with 5 times its weight of ordinary cyanide of potassium. Soak the fused mass in water; wash the kernels of metallic bismuth rapidly, first with water, then with weak alcohol and finally with strong alcohol; collect upon a small, tared filter, dry and weigh. In case oxide or oxychloride of bismuth be operated upon, the reduction is soon completed, at a low heat, but the sulphide requires more time and a higher temperature. When, on treating the fused mass with water, only metallic grains remain undissolved, the reduction may be deemed complete; but if in reducing the sulphide, there is left a quantity of the latter, in the form of black powder, mixed with the metal, this powder should be collected and again fused with a fresh quantity of cyanide of potassium. The crucible should be weighed before the experiment and after it; also in connection with the tared filter; for it sometimes happens that particles of porcelain torn off from the crucible during the process

of reduction, remain mixed with the metallic bismuth. The method yields good results. (H. Rose, *Poggendorff's Annalen*, **91**, 104, and **110**, pp. 136, 425).

Boiling Point.

To determine the boiling point of any substance, place a quantity of the liquid in a small, tubulated, long-necked glass retort; throw into the liquid two or three fragments of coke, each as large as a small pea, a globule of mercury, a few small scraps of platinum foil, or better, a piece of metallic sodium, in case the liquid under examination is a hydrocarbon. As much as 100 or 200 c. c. of the liquid should be taken, if it can be had. The presence of the coke or metal, to facilitate ebullition, is essential. In case no fragments of solid matter are placed in the retort, the liquid is not only liable to "bump" when heated, but even to boil at a higher temperature,—in the case of some liquids, 5° or 6° higher,—than its real boiling point.

Close the tubulure of the retort with a cork, to a perforation in which a thermometer has been fitted, in such manner that when the cork is pushed tightly into the tubulure the bulb of the thermometer shall extend into the liquid, and reach almost, but not quite, to the bottom of the retort. (Warren, *Amer. Journ. Sci.*, 1865, **40**, 222). To that part of the stem of the thermometer which projects above the cork, tie a second thermometer, in such manner that it can be slipped up or down without difficulty, and place a broad sheet of paper or pasteboard across the top of the cork to screen the upper thermometer from any heat which might radiate from the retort. Set the retort upon a wire gauze support, above a lamp, in such position that its neck shall incline slightly upwards; place a screen below the retort to protect its sides from being overheated, twist moistened cloths around the neck of the retort to keep it cool, and in case the liquid is easily volatile, place bits of ice upon the cloth. Finally heat the liquid until it boils steadily, and the mercury in the thermometer ceases to rise.* Some little time will often be required in order that that portion of the thermometer which projects above the cork may acquire the highest temperature which the boiling liquid can communicate to it. — In case the liquid boils at a lower temperature than that of the air, place the retort in a bath of ice-water, and gradually raise the temperature of the bath by means of a small lamp-flame. — Arrange the upper, moveable thermometer so that its bulb shall be in contact with the stem of the fixed thermometer, at a point midway between the upper end of the mercury column in that thermometer and the centre of the cork. Then note the height of the barometer and of both thermometers. As soon as the mercury has become stationary in the thermometer, remove the lamp for a moment from beneath the retort, turn the neck

of the retort downward, and connect it with a Liebig's condenser. Again place the lamp beneath the retort, and continue to boil the liquid until most of it has been distilled over out of the retort. In the course of a few seconds after the lamp has been replaced, the mercury in the thermometer will again become stationary. At that moment note the time and the height of the mercury in the thermometers, and repeat these observations at frequent intervals, until the distillation is finished. If the liquid under examination be pure, the height of the thermometer will scarcely vary from first to last. In case there are slight differences between the earlier and later observations, either the average of the several observations, or better, of those corresponding to the longest intervals of time, may be chosen. Any material differences between the several observations would of course indicate that the liquid under examination was a mixture of two or more substances of unlike boiling points.

In case the boiling point of a mixture, such as ordinary spirit, is to be determined, only the first observation, made when the neck of the retort is inclined upwards, is of value; for the strength, and consequently the boiling point of the spirit, would change if the liquid were subjected to distillation. The process of distillation above described, is to be omitted, therefore, when a mixture is tested.

The purpose of the upper or side thermometer is merely to determine approximately the mean temperature of that portion of the mercury column in the fixed thermometer, which is above the cork, in order to ascertain what amount of correction should be made to compensate for the cooling action of the air. The upper thermometer would be useless in case no portion of the mercury column were to project above the cork, for in that event the whole of the metal, being surrounded with the vapor of the boiling liquid, would have one and the same temperature. But when, as is usually the case, a part of the mercury rises above the cork, and is thus exposed to a lower temperature than that of the boiling liquid, the upper extremity of the column will stand at a slightly lower point than it would if no portion of the mercury had been cooled. The correction to be applied to the observed temperature T° , is found by means of the following formula:—

$$N(T-t)\delta,$$

in which t is the observed height of the upper, moveable thermometer, N the difference between T° and that degree of the thermometer scale which is situated at the middle of the cork; or, in other words, the length of the column of mercury which has been cooled to t° by contact with the air, and δ the coefficient of apparent expansion of mercury in the glass of which the thermometer is constructed. The value of δ may be taken as equal to 0.0001545. (H. Kopp, *Poggendorff's Annal.*, 1847, **72**.)

38). For example,—if a liquid is observed to boil at 171.3° ($=T$) and the 25th degree of the thermometer be at the middle of the cork, then N will equal $171.3^{\circ}-25^{\circ}=146.3^{\circ}$. And if the mean temperature of the external column of mercury were 43° ($=t$), as observed by the upper thermometer, then $T-t$ would equal

$$171.3 - 43 = 128.3.$$

The correction to be applied will consequently be

$$146.3 \times 128.3 \times 0.0001545 = 2.9,$$

and the boiling point of the liquid "corrected for external column of mercury," will be

$$171.3 + 2.9 = 174.2.$$

Since the boiling point of a liquid depends on the pressure to which the liquid is subjected, another correction must be applied in order to reduce observations made under the varying pressure of the atmosphere, to the values which would obtain if the atmospheric pressure were normal,—that is to say, equal to 760 millim. of mercury at 0° . It is customary, on this account, to apply a correction of $\pm 0.1^{\circ}$ C., for every 2.7 millim. that the mercury in the barometer stands above or below 760. Strictly speaking, the correction to be applied to the boiling point of a liquid observed under an atmospheric pressure other than the normal pressure, varies with the nature of the liquid; for equal alterations of pressure do not cause precisely equal changes in the boiling points of different liquids. The value above given, of 0.1° for a variation of pressure of 2.7 millim., has been deduced from direct determinations of the boiling point of water under different pressures, and is absolutely accurate for that liquid alone. But since the greatest variations which ever occur in the pressure of the atmosphere are relatively very small, they may, without any appreciable error, be regarded as affecting the boiling points of all liquids equally.

Boracic Acid is determined either indirectly; as Fluoborate of Potassium; or as Borate of Magnesium. [See finding list for Boron, in the Appendix].

Principle I. Power of expelling carbonic acid from Carbonate of Sodium.

Applications. Estimation of boracic acid in aqueous solutions free from all other substances, except ammonium. In case a heavy metal has been separated from boracic acid by precipitating with sulphuretted hydrogen, the method now in question may be employed for determining boracic acid in the filtrate, after the excess of sulphuretted hydrogen has been expelled, by passing a current of carbonic acid through the liquor. The filtrate must, however, contain no acid besides boracic acid.

Method. Weigh out 1 or 2 times as much pure, fused carbonate of sodium, as there is supposed to be boracic acid in the solution to be analyzed. Dissolve the carbonate in the

weighed solution, evaporate the mixture to dryness at a gentle heat, and carefully heat the residue until it fuses to a thin liquid. A quantity of carbonic acid, equivalent to the quantity of boracic acid present, will be expelled, and there will be left a mixture containing a known quantity of sodium, and unknown quantities of carbonic and boracic acids. Weigh the residue, and determine the amount of Carbonic Acid contained in it. From the difference between the quantity of carbonic acid in the carbonate of sodium taken, and that found in the residue, calculate the amount of boracic acid (H. Rose).

In case the proportion of boracic acid in the solution to be analyzed is 'known approximately, between 1 and 2 equivs. of carbonate of sodium should be taken for two equivalents of boracic acid. If this be done, all the carbonic acid will be expelled on heating, and we have only to deduct from the weight of the residue the weight of oxide of sodium taken, in order to find the weight of the boracic acid. Since the tumultuous escape of carbonic acid might occasion loss, it is best not to ignite the residue left by evaporation all at once, but after thorough drying, to project it by small portions into a red hot crucible. (Schaffgotsch, *Pogg. Ann.*, 107. 427).

Properties. It may be remarked, in this connection, that boracic acid cannot be determined by evaporating its aqueous or alcoholic solution to dryness, and weighing the residue; for though little volatile of itself, considerable portions of the acid are carried away by the aqueous or alcoholic vapor. The same remark applies to solutions to which an excess of oxide of lead, of ammonia-water, or of triphosphate of sodium, has been added.

In the cold, no carbonic acid is expelled by boracic from carbonate of sodium, and only a small quantity escapes during the evaporation of the aqueous solution. It is only when the dry mass is ignited, that the evolution of carbonic acid really begins.

Principle II. Power of expelling water from certain refractory hydrates; i. e., fixity and power of combining with bases to form fixed products.

Applications. Estimation of water in the hydrates of Na, K, Ba and Sr.

Method. Mix a weighed quantity of the substance to be examined, with a weighed quantity of powdered anhydrous boracic acid, more than sufficient to saturate the whole of the alkali. Fuse the mixture in a platinum crucible until all the water has been expelled, and weigh the cold product. The difference between the final weight and the sum of the weights of boracic acid and substance taken, will represent the weight of the water. (Pfaff, *Handbuch analyt. Chem.*, 1824, I. 117). The substance analyzed must either be free from carbonic and other volatile acids, or the proportion of these substances must be determined

in separate portions of the material. The process can hardly be capable of yielding absolutely accurate results, since, as is well known, boracic acid is somewhat volatile in an atmosphere of aqueous vapor. Compare *biBorate of Sodium*.

Principle III. Power of decomposing silicious minerals.

An old method employed by Davy, Gehlen and others, for the decomposition of refractory minerals in which alkalis were to be determined, deserves mention, though it has long since been superseded by the methods of fusing with alkaline earths, or treating with fluorhydric acid.

Davy fused the powdered mineral with twice its weight of boracic acid glass, for half an hour, in an intense fire; decomposed the fused mass with dilute nitric acid; evaporated to separate silica; precipitated with carbonate of ammonium; supersaturated with nitric acid and separated the boracic acid by crystallization from the nitrates of the alkalis. (Pfaff, *Handbuch analyt. Chem.*, 1824, **1**, 467). Pfaff proposed to separate the alkalis from the boracic acid by converting them into sulphates, and then washing out the last portions of boracic acid with alcohol.

Basic Borate of Magnesium.

Principle. Insolubility in water, and fixity when ignited.

Applications. Estimation of boracic acid in presence of alkalis.

Method. Neutralize the solution with chlorhydric acid, add enough double chloride of magnesium and ammonium, that at least 2 parts of magnesia may be present in the solution for 1 part of boracic acid, pour in some ammonia-water, and evaporate the mixture to dryness in a weighed platinum dish. If, on the addition of the ammonia-water, a precipitate falls which does not dissolve readily on warming, a new quantity of chloride of ammonium must be added to the mixture. From time to time during the evaporation, add a few drops of ammonia-water. Ignite the dry residue, and afterwards treat it with boiling water. Collect the insoluble mixture of borate and oxide of magnesium upon a filter, and wash it with boiling water, until the wash water ceases to give any precipitate when mixed with nitrate of silver. Mix the filtrate and washings with ammonia-water, again evaporate to dryness, ignite and wash with boiling water, as before. Place both the insoluble residues in the platinum dish, and ignite them for a long time as strongly as possible, in order to decompose the small quantity of chloride of magnesium which may still be mixed with the borate. Weigh the cold product, dissolve it in chlorhydric acid, and determine how much magnesia is contained in it by precipitating as Phosphate of Magnesium and Ammonium, or estimate the magnesia at once by the process of Alkalimetry. Subtract the weight of the magnesia

found from the weight of the borate of magnesium, in order to obtain the weight of the boracic acid. The process yields satisfactory results. (Marignac, *Zeitsch. analyt. Chem.*, **1**, 406).

Precautions. The platinum dish must be weighed in the first place, since small portions of platinum are apt to appear on dissolving the residual borate in chlorhydric acid. If the weight of the dish were unknown, it would be necessary to weigh this abraded platinum, and subtract its weight from that of the borate of magnesium. When the volume of liquid to be operated upon is considerable, it had better be concentrated to a small bulk in a porcelain dish, and afterwards evaporated to dryness in the platinum vessel. — In case boracic acid is to be separated from a heavy metal precipitable by sulphuretted hydrogen, the filtrate from the metallic sulphide should be mixed with hydrate and nitrate of potassium, evaporated to dryness and ignited, before adding the chloride of magnesium, as above described.

Borate of Potassium. See *Borate of Sodium*.

Borate of Sodium.

Principle. Solubility in water.

Applications. Separation of boracic acid from most of the metals, other than alkali metals.

Method. Boil or fuse the borate to be analyzed with carbonate or hydrate of potassium, or of sodium, filter off the precipitated carbonate or hydrate of the metal, and determine boracic acid in the filtrate as *Borate of Magnesium*, or as *Fluoborate of Potassium*.

BiBorate of Sodium. (Borax).

Principle. Power of expelling Carbonic, Nitric and Silicic acids, when fused with salts of these acids. See the respective acids and *Boracic Acid*.

It is to be observed, that though "borax-glass" may be kept fused at a red heat for quarter or half an hour without loss, through volatilization, an appreciable quantity of the compound exhales at a white heat. A decided loss of weight occurs, for example, when a platinum crucible containing dry borax-glass is ignited even for a few minutes at the blast lamp. (Fresenius, *Zeitsch. analyt. Chem.*, **1**, 65).

Borax was formerly somewhat used for decomposing refractory minerals. Thus Berzelius & Hisinger (*Gehlen's neues Journ. der Chemie*, **6**, 304) fused finely pulverized spinel with twice its weight of borate of potassium, in a platinum crucible, and dissolved the fused mass in chlorhydric acid. (Compare *Aluminate of Sodium*). — Borax-glass is still used, in conjunction with carbonate of sodium, in the excellent method of Plattner (*Probirkunst mit dem Löthrohre*, 1853, p. 689), for analyzing, with the aid of the mouth blowpipe, those iron ores which cannot be decomposed by acids. It is to be observed, however, that the process

depends upon the fusibility of borate of iron, and the solubility of this substance in acids rather than upon any superior affinity of boracic acid for iron. The details of the method are as follows:—Grind a considerable quantity of the ore to fine powder, best in an agate mortar, mix the powder thoroughly, spread it to a thin layer, and draw a fair sample of it by taking a number of small quantities from different parts of the layer. Dry the sample at 100° , weigh out 0.1 gram. of the powder on a delicate assay balance, transfer it to a large test tube, and pour upon it, little by little, a quantity of strong chlorhydric acid. As soon as the acid has ceased to act in the cold, heat it over a spirit lamp as long as anything dissolves; throw the mixture upon a small filter, and wash the residue with boiling water. Dry the residue, which will exhibit a yellowish, red, or gray color, over a spirit lamp. If the ore were of such character as to be decomposed completely by chlorhydric acid, the residue upon the filter would be colorless, and free from iron; so that the process now in question, *i. e.*, the fusion with borax, would not be called for. But the residue does, in fact, contain silicates of iron and the earths, as well as quartz, and rarely some sulphate of barium, also. As soon as it is thoroughly dry, mix it in the filter with as much powdered borax-glass, and 3 times its bulk of dry carbonate of sodium. Roll the paper into the form of a small ball or cylinder, place the ball in a hole bored across the grain of a good piece of charcoal, and melt the mixture, with the oxidizing blowpipe flame, to a clear, transparent bead. After the bead has become cold crush it in a steel mortar, place the powder in a light porcelain cup covered with a watch glass, and treat with dilute chlorhydric acid; then evaporate the solution to dryness, together with the previous solution obtained by acting upon the ore with acid, to separate Silicic Acid. The filtrate from silicic acid is boiled with nitric acid to oxidize the iron; the latter is precipitated, together with alumina, as Hydrate of Iron, and the alumina dissolved out as Aluminate of Sodium, in the usual way. — The process has great merit from its simplicity. It may be put in practice almost anywhere, since it neither requires a well appointed laboratory nor expensive apparatus. It is evident that besides iron, silicic acid, and many other constituents of refractory silicates, may readily be determined in this way. Analyses of red ochre, made under my direction by this method, and by a modification of it, in which either pure silicic acid or silicate of sodium (water glass) was substituted for the borax, showed clearly the importance of the borax, and the impropriety of trying to do without it.

To prepare borax-glass, heat ordinary crystallized borax in a platinum or porcelain dish until it ceases to swell up. Grind the porous

residue to powder, and again heat it in a platinum crucible, until it fuses to a transparent mass. Pour the semi-fluid, viscid substance upon a piece of porcelain, and keep the cold solid in a well-stoppered bottle. The borax-glass must, in most cases, be reheated just before use to ensure its absolute freedom from moisture.

The purity of commercial borax may be tested by adding carbonate of sodium to the aqueous solution, and by adding solutions of nitrate of barium and nitrate of silver to other portions of the solution after acidulating it with nitric acid. Neither of these reagents should occasion any alteration in the appearance of the solution. In case the borax is impure, it may be purified by recrystallization.

Bromates may be converted to Bromides by ignition, and weighed as such; or they may be mixed with an excess of chlorhydric acid, the mixture evaporated to dryness, and the chlorine estimated as Chloride of Silver, by titration. From the weight of chlorine found, the equivalent weight of bromic acid may then be calculated. (Mohr).

Bromides of volatile elements, such as the bromides of arsenic, antimony, phosphorus and sulphur, are completely decomposed by water, with formation of bromhydric acid, which may be determined by precipitation, as Bromide of Silver.

Bromide of Mercury.

Principle. Power of Oxide of Mercury to absorb bromine at the ordinary temperature, and fixity of the compound formed.

Application. Estimation of bromine in organic substances.

Method. Heat the substance to be analyzed in a stream of hydrogen, and burn the hydrogen thus charged with the vapor or products of distillation of the substance, in a stream of oxygen. Pass the products of the combustion over a layer of strong sulphuric acid, to free them from water, absorb the bromine in a tube filled with fragments of precipitated oxide of mercury, and the carbonic acid in potash lye. The oxide of mercury should be in the form of pellets, or coarse masses, and should be followed by a short column of chloride of calcium, placed at the end of the tube farthest from the burning hydrogen. For the details of the process see A. Mitscherlich's paper in *Zeitsch. analyt. Chem.*, 1867, 6. pp. 151, 153, 156, 141. Compare Carbon, oxidation of with oxygen gas.

Bromide of Silver.

Principle 1. Insolubility in water and nitric acid.

Applications. Separation of bromine from most of the metals, and from organic substances. Estimation of bromhydric acid and of free bromine. Separation of bromhydric acid from As_2O_3 , As_2O_5 , P_2O_5 , CrO_3 , SO_3 , B_2O_3 , $\text{C}_2\text{H}_2\text{O}_4$, HFl , SiO_2 and CO_2 .

Since bromide of silver is precipitated before

chloride of silver when nitrate of silver is added to a cold solution containing both chlorides and bromides, the insolubility of the bromide may even be used for separating bromine from chlorine as will be described below.

The *Methods and Precautions* are similar to those described under Chloride of Silver. The process yields excellent results.

Properties. As prepared in the wet way, bromide of silver is a yellowish-white precipitate, insoluble in water and nitric acid, tolerably soluble in ammonia-water and readily soluble in solutions of the hyposulphites and cyanides of alkali-metals. Though insoluble in very dilute solutions of alkaline chlorides and bromides, some of it dissolves in concentrated solutions of these salts. Traces of it dissolve also in solutions of the alkaline nitrates. A solution of iodide of potassium converts it into iodide of silver. — When heated, it melts to a reddish liquid which solidifies to a yellow, horn-like mass on cooling. It may be weighed, however, as well after having been dried at 100° as after melting. When heated in chlorine gas it is converted into chloride of silver and when heated in hydrogen to metallic silver. The precipitated bromide gradually becomes gray and finally black when exposed to light. Both the precipitated and the fused bromide are decomposed by metallic zinc with formation of metallic silver. The composition of the bromide is as follows: —

Ag	=	108	—	57.44
Br	=	80	—	42.56
		188		100.00

Determination of Bromine in bromides of Organic Substances soluble in water. [Compare Chloride of Silver and Iodide of Silver]. Weigh out about 1 gram. of nitrate of silver, dissolve it in water and add chlorhydric acid until all the silver is precipitated as chloride. Wash the chloride of silver with hot water, by decantation, and pass the washings through a small weighed filter to retain any suspended particles of the chloride. Pour upon the washed mass of chloride of silver an aqueous solution of about 0.5 gram. of the substance to be analyzed. Warm the mixture and let it stand for a couple of hours, then collect the mixed bromide and chloride of silver upon the weighed filter, above mentioned, wash it thoroughly, dry, and weigh. From the weight of the mixed precipitate and the known weight of silver taken, calculate the weight of the bromine in the precipitate as explained below, under Principle III.

One merit of the process, at least as applied to rare and costly substances, consists in the fact that the substance is not destroyed. It is found again in the filtrate from the bromide of silver in the form of a chloride. The process is not applicable to all organic substances containing bromine. Only that portion of bromine (as

in a bromide) which is precipitable by nitrate of silver can be thus determined, but on this very account the process is valuable for determining the rational constitution of certain bromine compounds. (Maly, *Zeitsch. analyt. Chem.*, 1866, 5. 68; Kraut, *Ibid.*, 1865, 4. 167).

Separation of Bromine from Chlorine. [Compare Chloride of Silver and Iodide of Silver]. Several methods of separating bromine from chlorine depend upon the principle now in question.

A. Fehling's method. Mix the cold solution to be analyzed with a quantity of nitrate of silver solution somewhat more than sufficient to precipitate all the bromine, but not nearly sufficient to throw down all the chlorine. Shake the mixture strongly and leave it standing for some time, with occasional agitation. Wash the mixed precipitate of bromide and chloride of silver with especial care and thoroughness, dry, ignite, weigh, and treat a weighed portion of the residue with chlorine, as directed below, under Principle III, or with zinc (see Silver). To find the quantity of chlorine, precipitate another weighed portion of the original solution completely with nitrate of silver and from the weight of this precipitate deduct that of the bromide of silver found. — The following rule indicates in a general way how much nitrate of silver should be used. If the solution to be analyzed contains 0.1 per cent of bromine, add $\frac{1}{10}$ or $\frac{1}{8}$ as much of the solution of nitrate of silver as would be required to effect complete precipitation; — if 0.01 per cent, $\frac{1}{10}$; — if 0.002, $\frac{1}{8}$; — if 0.001, $\frac{1}{60}$. (Fehling, *Journ. prakt. Chem.*, 45. 269).

B. Mohr's method. Precipitate all the bromine and part of the chlorine by means of a known weight of silver, added in the form of nitrate of silver. Wash and weigh the mixed precipitate. Calculate the amount of chloride of silver equivalent to the metallic silver taken, subtract this weight from that of the mixed precipitate and finally calculate how much bromide of silver was present, by the method given below, under Principle III. — This method has the merit of being more convenient and expeditious than the old method with chlorine described below (Principle III), but is probably somewhat less accurate than the latter, especially when the proportion of bromine in the mixture is small. In criticising the process, Fresenius urges that the supposition that a weighed quantity of silver will yield a precisely equivalent quantity of chloride of silver is practically incorrect, errors to the extent of some milligrammes being scarcely avoidable; it might thus happen that bromine could be calculated from a supposed difference even in cases where no trace of this element was present. (Compare Principle III).

The silver used as the precipitant may either be weighed in the metallic state and then be dissolved in nitric acid, or it may be added in

the form of a standard solution of nitrate of silver. (F. Mohr, *Ann. Chem. und Pharm.*, 93, 76).

C. Wittstein's method. See under Chloride of Silver.

D. Pisani's method. Add to the mixed solution of bromides and chlorides a known quantity of a standard solution of nitrate of silver in slight excess, filter and determine the silver in the filtrate by titration with iodine. (See Iodide of Silver). The precipitate is weighed and the proportion of bromine calculated as in B. The principle of the method is slightly different from that of the preceding methods, inasmuch as it precludes the partial precipitation. (Pisani, *Comptes Rendus*, 44, 352).

Principle II. Reduction of to metallic silver by hot hydrogen.

Applications. Estimation of bromine in presence of chlorine.

Method. Weigh out a portion of the mixed precipitate of bromide and chloride of silver in a light bulb-tube: pass a slow current of hydrogen through the tube, heat the substance in the bulb until it fuses, and occasionally shake the fused mass so that new surfaces may be exposed to the action of the hydrogen. When the reduction seems to be complete, allow the tube to cool, hold it in an inclined position for a moment so that the hydrogen within it may be replaced by air, weigh it, again heat its contents in a current of hydrogen and continue these operations until the two last weighings agree. Calculate how much chloride of silver is equivalent to the metallic silver found, subtract this chloride of silver from the weight of the mixed chloride and bromide of silver taken, and calculate how much bromine was present, by the method given below, under Principle III. This method of reducing by hydrogen offers an excellent control to the method by chlorine described below, under Principle III. — Compare also the details of manipulation there described.

Principle III. Conversion into chloride of silver by hot chlorine. [Compare Chloride of Silver, decomposition of by bromide of potassium].

Applications. Estimation of bromine in presence of chlorine.

Method. After the mixed precipitate of bromide and Chloride of Silver has been collected and weighed in the usual way, fuse it in the crucible and pour out upon a piece of porcelain as much of the fused mass as will be sufficient for an analysis. Place the fragments in a weighed bulb tube, and again weigh the tube with its contents. Pass a slow stream of pure, dry chlorine gas through the tube, heat the silver salts to fusion and shake the bulb occasionally, in order to expose fresh surfaces of the fused mass to the chlorine. After the lapse of 20 or 30 minutes, allow the tube to cool, detach it from the chlorine generator, hold it in an oblique position until the

chlorine has been replaced by air, and weigh. Again heat the contents of the tube in a current of chlorine during 10 or 12 minutes and weigh as before. Repeat the operations of heating and weighing until two consecutive weighings give the same result. The decrease of weight is simply the difference between the weight of the bromine originally present in the mixed salts and that of the chlorine which has replaced it. The weight of bromine originally present is therefore deduced from the proportion.

$$\frac{\text{Difference between At. Wts. of Cl and Br}}{44.5} = \frac{\text{At. Wt. Br}}{80} = \frac{\text{Decrease of Weight}}{\text{Amt. of Br present.}}$$

It results from this proportion that the weight of bromine may be obtained by multiplying the observed decrease by 1.797. If the amount of chlorine originally present is also desired, calculate the quantity of silver in the pure chloride of silver last weighed, and subtract this weight of silver and the weight of bromine deduced as above described, from the original weight of the mixed chloride and bromide. The remainder is the required amount of chlorine. — To determine the quantity of chlorine, precipitate completely with nitrate of silver a new portion of the substance to be analyzed and deduct from the weight of this precipitate that of the bromide of silver found as above.

Precautions. Though the method is tedious and inconvenient, very accurate results can be obtained by it if the proportion of bromine in the mixture is not too small. Care must be taken to expel the last traces of bromine and to weigh with scrupulous accuracy in each instance. The method is less liable to error than Mohr's process of precipitating with a known weight of silver, above described, (under Principle I). According to Fresenius, a simple experiment will show that pure chloride of silver heated cautiously in a current of chlorine in a light bulb tube suffers no alteration of weight. An error of 0.5 milligramme in this operation would be more surprising than an error of 2 mgrs. in the conversion of 2 or 3 grms. of silver into chloride of silver, more especially if a filter were used in the process; and the filter can hardly be dispensed with, since a precipitate almost always subsides less readily and completely in case of partial precipitation than when the precipitation is complete.

The process is not directly applicable for determining small traces of bromine in presence of large quantities of chlorine, as in the waters of saline springs, for example. In such cases the bromine must be concentrated either by fractional precipitation with nitrate of silver, as has been described above (Principle I), by fractional solution (see Bromide of Sodium), or by fractional distillation (see Bromine).

It is easy to control the results obtained by this method by treating the residual chloride

of silver with hydrogen, as described under Principle II. The difference between the weight of the mixed bromide and chloride of silver, and the amount of chloride of silver equivalent to it found in the direct way by the method now in question, and by calculation in the method by hydrogen, should be the same.

Bromide of Potassium.

Principle. Power of decomposing freshly precipitated chloride of silver.

Application. Separation of Bromine, Iodine and Chlorine.

Method. See Iodide of Potassium.

Bromide of Sodium.

Principle. Solubility in strong alcohol.

Applications. Separation of bromine from chlorine, or rather concentration of bromine when mixed with chlorides.

Method. Add an excess of carbonate of sodium to the mixed solution of bromides and chlorides, filter if need be, evaporate nearly to dryness, and extract the residue with hot absolute alcohol. The whole of the bromide of sodium [or of potassium] will dissolve together with a small portion of chloride of sodium. Add to the solution a drop or two of a solution of carbonate of sodium, evaporate to dryness, dissolve the residue in water, acidulate with nitric acid, precipitate with nitrate of silver and analyze the mixture of bromide and chloride of silver, as described under Bromide of Silver. (Compare Marehand, *Journ. prakt. Chem.*, 47. 363).

Bromine is commonly determined as Bromide of Silver, or as Bromine (by volumetric and colorimetric methods, or by loss). [See the finding list in Appendix].

Principle I. Volatility.

Applications. Estimation of bromine in metallic bromides. Separation of bromine from chlorine, or rather concentration of bromine when mixed with chlorides.

Method A. Place the dry weighed bromide in a porcelain crucible, mix it with pure sulphuric acid in slight excess, and evaporate until no more fumes are seen to arise from the dry residue. Weigh the residual metallic sulphate, calculate the amount of metal in this sulphate and subtract it from the weight of the bromide taken; the difference gives the weight of bromine in the sample analyzed. The method is inapplicable for the analysis of the bromides of silver, lead, mercury and tin, since these compounds are not readily decomposed by sulphuric acid. — Platinum crucibles cannot be employed; the metal would be attacked by the escaping bromine.

Method B. Supersaturate the bromide to be analyzed with chlorhydric acid, evaporate to dryness to expel the excess of acid, and estimate the chlorine in the residue as Chloride of Silver, by titration. From the weight of chlorine found calculate the equivalent weight of bromine. (Mohr).

To concentrate bromine when mixed with a

large proportion of chlorides, mix the solution in a flask with chlorhydric acid and binoxide of manganese, connect the flask with two wide Woulfe bottles, by means of bent delivery tubes. Charge the bottles with strong ammonia-water and slowly heat the mixture in the flask. The whole of the bromine will pass over before much, if any, chlorine is evolved. The bottles must be large enough and the distillation slow enough that no vapors shall escape. When all the bromine has been evolved, as may be seen by the color of the gas in the tubes and in the flask above the liquid, loosen the cork of the flask to prevent the return of bromide of ammonium fumes, let the bottles cool and unite their contents. The liquid, which contains all the bromine in the substance analyzed, together with a relatively small proportion of chlorine, may then be analyzed by one of the methods described under Bromide of Silver.

Principle II. Power of decomposing iodide of potassium and other metallic iodides.

Applications. Estimation of free bromine (Method A); estimation of iodine in presence of bromine and chlorine (Method B).

Method A. Bring the gaseous bromine or the bromine water to be analyzed into contact with a solution of iodide of potassium and determine how much iodine is set free, by titrating with a standard solution of hyposulphite of sodium, sulphurous acid, arsenite of sodium or some other reducing agent (see Iodine). One equivalent of iodine is set free by each equivalent of bromine in the substance analyzed.

If bromine water is to be tested, the portion to be analyzed may be measured in a pipette provided with a tube charged with moist hydrate of potassium, to protect the lungs of the operator, and the liquid may simply be stirred into a solution of 1 part iodide of potassium in 10 parts of water. The formation of a black precipitate of iodine in the liquid would indicate that an insufficient quantity of iodide of potassium had been taken. — If the bromine is evolved in the form of gas, it may be collected in a series of two or three small flasks, or miniature Woulfe bottles charged with the solution of iodide of potassium and tightly connected with one another and with the generating flask. At the mouth of the flask in which the bromine is generated, it is well to have a wide bulb tube, slanting back towards the flask, in order to condense aqueous vapor and return it to the flask. — The method yields accurate results and is easily executed.

If the solution to be analyzed contains bromhydric acid or a metallic bromide, as well as free bromine, determine the free bromine in a weighed portion of it with iodide of potassium as above described. Mix another portion with an excess of sulphurous acid in aqueous solution, allow the mixture to stand for some time,

acidulate with nitric acid and determine the whole of the bromine as Bromide of Silver. The difference between the two determinations gives the weight of the combined bromine.

If the bromine under examination contains chlorine, the proportion of the two elements may be determined as follows:—Let A represent the weight of the impure bromine taken, i the weight of the iodine found, y the weight of the chlorine in A, and x that of the bromine in A, then

$$y = \frac{i - 1.6366 A}{1.091}; \text{ and } x = A - y,$$

(Bunsen, *Annal. Chem. und Pharm.*, 86. 276).

Method B. Prepare a standard solution of bromine by dissolving 1 grm. of bromine in 4 litres of water. At the moment of use place 40 c. c. of this solution (= 0.01 grm. of bromine) in a litre flask and dilute with water to the mark (see Alkalimetry) in order to obtain a solution containing $\frac{1}{100}$ milligramme of bromine in each cubic centimetre. If the iodide solution to be tested is alkaline, neutralize it with dilute nitric acid, then add to it, by means of a graduated pipette, a definite number of drops (say one c. c.) of bisulphide of carbon or of chloroform and from another pipette or burette pour upon the mixture a stated number of drops of the weak bromine water. On shaking the mixture the bisulphide of carbon or the chloroform will dissolve the iodine which has been set free and will become violet-colored. As soon as the color ceases to become deeper on shaking the mixture after the addition of a drop of the bromine water, remove the colored bisulphide with a pipette and replace it with a fresh quantity, equal to that first taken, add a further portion of the bromine water, and continue to repeat these operations until the last portion of bisulphide or of chloroform fails to become violet-colored after the addition of the bromine. The quantity of standard bromine water used, minus the last portion which failed to impart any violet color to the test liquid, is equivalent to the amount of iodine in the substance tested. — Both bisulphide of carbon and chloroform are capable of indicating the presence of exceedingly minute traces of free iodine. Bromine alone colors bisulphide of carbon yellow. An excess of bromine in presence of iodine yields bromide of iodine which imparts no violet color to the bisulphide. In order to judge of the intensity of the coloration, similar amounts of the bisulphide should be added throughout the experiment. (De Luca, *Comptes Rendus*, 37. 866). According to Fresenius this method is neither so convenient nor so practical as the analogous method of Dupré, in which Chlorine is used in place of bromine.

According to Casaseca (*Ann. Ch. et Phys.*, (3), 45. 482) the method above described is faulty, inasmuch as bromine water decomposes

rapidly. A standard solution of it cannot be kept during 24 hours. He finds, moreover, that the amount of iodine set free is not always equivalent to the quantity of bromine used; in one experiment as much as three equivalents of bromine were required to liberate the iodine. Before proceeding to the actual analysis he therefore determines empirically the value of his bromine water by titrating with it a known weight of iodide of potassium. In case iodine is to be determined in solutions containing but little more than 1 milligramme of the element in 10 c. c., a standard solution of iodide of potassium is first prepared of such strength that each c. c. of it shall contain 1 milligramme of the iodide. 1 c. c. of this solution is placed in a graduated tube, diluted with water to 10 c. c. and tested with chloroform and bromine water, according to De Luca's directions. The bromine water should contain about 1 milligram of bromine to the c. c. and had better be poured from a burette marking tenths of cubic centimetres. The quantity of bromine water which represents 1 milligram of KI, or the 0.000763 grm. I, therein contained, having thus been determined, the actual analysis of any unknown iodide solution of the given strength may be undertaken. A similar method of procedure is applicable to solutions containing less than 0.5 milligramme of iodine in 10 c. c.; but in that case two standard solutions of bromine water are needed, the one containing 1 milligram of bromine and the other 10 milligrams to the c. c. The strength of any unknown solution must be determined approximately by a preliminary trial.

In case bromine, chlorine and iodine are all to be determined, De Luca precipitates one portion of the solution completely with a standard solution of nitrate of silver (see Chloride of Silver); determines the iodine as above described in another portion, and the bromine and iodine together in a third portion by means of a standard solution of Chlorine.

Principle III. Power of oxidizing the lower oxides of iron, manganese, and some other metals, ferrous salts, sulphurous acid, hyposulphites, etc., etc.

Applications. Precipitation of manganese as binocide. Estimation of free bromine, either in aqueous solution or in the gaseous form. Estimation of free bromine in presence of chlorine.

Methods. Similar to those described under Chlorine. For precipitating binOxide of Manganese, in particular, from acetic acid solutions, and for oxidizing manganous salts before precipitating the metal as Hydrate of sesquioxide of Manganese, bromine will be found (after Henry) to be a much more convenient agent than chlorine. — In case free bromine contaminated with chlorine is to be estimated, weigh out some of the substance in a small glass bulb, treat it with a cold aqueous

solution of sulphurous acid and precipitate with nitrate of silver. Digest the mixed precipitate of bromide and chloride of silver with nitric acid to dissolve any sulphite of silver which may have gone down, wash, dry and weigh. — If A equal the weight of substance taken, B that of the AgCl plus AgBr obtained, x the weight of bromine in the substance taken, and y the weight of the chlorine, then

$$y = \frac{B - 2.25A}{1.635}; \text{ and } x = A - y.$$

(Bunsen, *Annal. Chem. und Pharm.*, 86. 276).

Principle IV. Decoloration of by oil of turpentine (substitution of Br for H in the oil).

Application. Estimation of free bromine.

Method. Dissolve 20 grammes of perfectly pure oil of turpentine in enough absolute alcohol that the mixture may be equal to 200 c. c. 34 c. c. of this liquid (= 1 equivalent of oil of turpentine) correspond to 8 grms., or 1 equivalent, of bromine. Place the solution of bromine to be analyzed in a stoppered bottle, add the oil of turpentine solution drop by drop, shaking the bottle after each addition, until the mixture has become perfectly colorless. One equivalent of oil of turpentine takes up and decolorizes 1 equivalent of bromine. The process yields satisfactory results, but is less convenient than the method with iodide of potassium (see Principle II). In case very small quantities of bromine are to be estimated, a more dilute solution of oil of turpentine should be used than that given above.

Principle V. Power of decomposing ammonia with evolution of nitrogen. (See Nitrogen Compounds).

Principle VI. Power of coloring ether, water, and chloroform.

Applications. Estimation of bromhydric acid or combined bromine, even in presence of chlorides. Especially useful for determining small quantities of bromine.

Methods. See Chlorine, power of decomposing metallic bromides.

Principle VII. Affinity for metals of the alkalis and alkaline earths at high temperatures.

Application. Estimation of bromine in organic substances.

Methods. Ignite the substance with quicklime, or the like, dissolve the resulting bromide of calcium in water and precipitate Bromide of Silver. For the details of the ignition see Chlorine.

Brucein. [Compare Iodo-mercurate of Brucein.]

Principle. Solubility in benzole.

Application. Separation of brucein from strychnin.

Method. See Strychnin.

Cadmium may be determined as Oxide, Sulphide or Carbonate, or as metallic

cadmium. For the separation of cadmium from other elements see finding list in the Appendix.

Principle. Insolubility in dilute acids when in presence of metallic zinc.

Method. Place a rod of pure zinc in the dilute sulphuric, chlorhydric, or even nitric acid solution of the cadmium compound, wash the precipitated cadmium with hot water, dry (best in an atmosphere of some nonoxidizing gas), and weigh. (*Pfaff, Handbuch analyt. Chem.*, 1825, 2. 391; Meissner, *Gilbert's Annalen*, 49. 99). According to Wollaston (*Schweigger's Jahrb.*, 4. 371), it is best, after any heavy metals which may be present have been thrown down by iron and separated by filtration, to put the chlorhydric acid solution of cadmium, etc., in a platinum dish with a piece of zinc. The metallic cadmium will in this case adhere firmly to the platinum and may consequently be washed with peculiar ease. It may either be weighed as such, after drying, or dissolved in chlorhydric acid and reprecipitated as Carbonate of Cadmium.

Calcium may be determined as Carbonate, Oxide, Oxalate, or Sulphate. For its estimation by alkalimetric methods see the Carbonate, Oxalate and Oxide. For the separation of calcium from each of the other elements see finding list in the Appendix.

Cantharidin.

Principle. Sparing solubility in bisulphide of carbon, and in alcohol.

Applications. Separation of cantharidin from fats and oils. Estimation of cantharidin in Spanish flies.

Method. Plug the throat of a funnel or percolation cylinder with cotton wool, pour fine sand upon the cotton to the depth of 10 or 15 m. m., and place about 40 grms. of finely powdered cantharides above the sand. Exhaust the powder thoroughly and methodically with ether or chloroform. Evaporate the solution to dryness and heat the residue, at a temperature no higher than 40° , until it ceases to smell of the ether or chloroform. Allow the residue to cool and pour upon it 50 or 60 c. c. of bisulphide of carbon. When the mass becomes pulverulent, transfer it to a weighed filter and wash the crystals of cantharidin with bisulphide of carbon until the last traces of oil have been removed. Finally dry and weigh the filter with its contents. (Mortreux, *Journ. Pharm. et Chim.*, 46. 33).

Dragendorff & Blum (*Zeitsch. analyt. Chem.*, 1867, 6. 126) mix 25 or 30 grms. of powdered cantharides with 8 or 10 grms. of calcined magnesia, moisten the mixture with water and rub it to a paste. The paste is then dried on a water bath, the dry product rubbed to powder and enough dilute sulphuric acid added to slightly supersaturate the magnesia. Immediately after adding the acid the mixture is shaken with small successive quantities of ether as long as any cantharidin continues to

be dissolved. The several ethereal solutions are mixed, the mixture is shaken with water and the ether recovered by distillation. The residue from the distillation, — consisting of crystals of cantharidin, fat and a yellow substance, — is transferred to a tared filter and washed first with bisulphide of carbon to remove fat, and afterwards with alcohol to dissolve the yellow substance. The cantharidin is then dried at 100° and weighed. Corrections should be applied to compensate for the solubility of cantharidin in bisulphide of carbon and in alcohol, as follows: — For every 10 c. c. of bisulphide of carbon used add 0.0085 grm. to the amount of cantharidin actually weighed, and for every 10 c. c. of alcohol add 0.0024 grm. — Instead of magnesia, oxide of zinc may be used; and, instead of extracting at once with ether, the slightly acid mixture of sulphate of magnesium, sulphuric acid and cantharides may be evaporated to dryness and the dry mass extracted with ether or with chloroform. No cantharidin is lost by volatilization during the distillation of the ethereal solution.

Carbon. [Compare Graphite; see also Nitrogen and Oxygen].

Principle I. Insolubility in dilute chlorhydric acid,¹ or in solutions of sulphate of copper, chloride of copper, chloride of iron, or acidulated chromate of potassium.

Application. Separation of carbon from iron; — as in the analysis of cast-iron and steel.

Method A. Solution of the iron in dilute chlorhydric acid, with the aid of a weak galvanic current.

Cast-Iron. In case the material to be operated upon is white or gray cast-iron, weigh out a lump (10 or 15 grms.) of the iron and suspend it in dilute chlorhydric acid by means of platinum-pointed pincers, in such manner that that portion of the mass which is in contact with the platinum shall not be moistened by the acid. Or, in default of pincers, lay the iron upon a small sieve of platinum and sink the sieve in the dilute acid. The dilute acid may be prepared by mixing about 12 vols. of water

with 1 vol. of chlorhydric acid of 1.12 sp. gr. Connect the pincers with the positive pole of a single Bunsen element, by means of a copper wire. Immerse a strip of platinum foil in the dish of chlorhydric acid and by means of another wire attach it to the negative pole of the element. Regulate the strength of the galvanic current in such wise that no sesquichloride of iron shall be formed. That is to say, increase or diminish the distance between the electrodes. To do this, move the foil away from or towards the lump of iron. The presence of any ferric chloride is, for that matter, immediately made manifest by the yellowish tinge which it imparts to the stream of concentrated ferrous chloride flowing downward from the piece of iron. During the process of solution the external appearance of the lump of iron undergoes but little change, for the carbon and other insoluble matter retains the original form of the lump.

After about 12 hours, when all the iron which was immersed in the acid has dissolved, break off from the mass of carbon the compact piece of iron which has been nipped by the pincers, wash, dry and weigh it, and subtract its weight from that of the original lump of iron, in order to obtain the weight of iron which has really dissolved. Collect the carbon and other insoluble matter upon a tared filter of asbestos, wash with hot water, dry at 120° – 130° in a current of air, and weigh. Transfer the dry residue to a weighed porcelain boat, rinse out the filtering tube with dry oxide of mercury and pour the rinsings upon the carbon in the boat. Place the boat in a glass tube behind a column of oxide of copper, heat the latter to redness, ignite the contents of the boat in a current of oxygen gas, in the manner explained below (Principle II), and collect the Carbonic Acid in a weighed quantity of potash lye or soda-lime. An unweighed chloride of calcium tube may be employed to catch the vapor of mercury. Finally weigh the incombustible residue of slag and silica in the boat. — The process yields good results as compared with most other processes, and has the very great advantage of dispensing with the necessity of reducing the iron to powder.

Precautions. Care must be taken to maintain a weak galvanic current. The iron should dissolve as protochloride and all the hydrogen should escape from the surface of the platinum foil. Little or no gas should be evolved from the surface of the lump of metal. A strong current of galvanism would not only be apt to render the iron passive, but might occasion an evolution of chlorine from the surface of the iron, whereby some of the carbon would be oxidized and lost as carbonic oxide or carbonic acid. Another portion of the carbon would unite with chlorine, and the compound being subsequently decomposed by the galvanic current, carbon would be set free at the negative pole, together with hydro-

¹ For an account of the liquid and gaseous hydrocarbons which may be formed by the action of dilute acids upon white and gray cast-iron, see Hahn, *Annalen Chem. und Pharm.*, 129. 57. See also Rinman, *Zeitsch. analyt. Chem.*, 1865, 4. 159, who finds that pieces of thoroughly hardened steel leave no carbonaceous residue when treated with chlorhydric acid of 1.12 sp. gr., and that the carbon which separates from soft steel can all be destroyed by dissolving the steel in boiling chlorhydric acid of 1.12, and continuing to boil the mixed acid and residue for half an hour after the metal has dissolved. On the other hand, a considerable residue of carbon insoluble in hot acid is left when soft steel is slowly dissolved in cold chlorhydric acid. Sulphuric acid diluted with 5 parts of water yields results similar to those obtained with chlorhydric acid, only the sulphuric acid must be boiled rather more vigorously than the chlorhydric in order that all the carbon shall be expelled as a hydrocarbon gas.

gen, in such manner that some of it might be lost in the form of a hydrocarbon gas.

The points of contact between the platinum pincers and the lump of metal must not be allowed to become moist lest the current be impeded by the separation of a film of carbon between the platinum and the iron (Weyl, *Pogg. Ann.*, **114**, 507).

The process as above described succeeds well with specular iron, according to Weyl and Fresenius (*Zeitsch. analyt. Chem.*, 1864, **3**, 337, note).

Steel. In the case of steel a new precaution is required, since the carbon, which separates when steel is dissolved in this way, is so finely divided that the particles do not cohere and remain as a permanent mass at the positive pole of the battery. If the operation were conducted as above described most of the carbon would be transported to the negative pole of the battery, there to be deposited in part and in part to be lost through union with the nascent hydrogen and evolution as carburetted hydrogen gas. To prevent this waste of carbon, a porous membrane must be interposed between the fragment of steel and the negative pole of the battery. The apparatus may be prepared as follows:—Tie a piece of bladder over one end of a wide glass tube or broken cylinder, support the cylinder in a beaker half full of dilute chlorhydric acid, so that the bladder end shall be immersed in the liquid near the bottom of the beaker, and pour dilute chlorhydric acid into the cylinder until the acid stands at sensibly the same level within and without. Hang the weighed lump of steel in the acid in the cylinder, immerse the platinum foil which serves as the negative pole of the battery in the acid in the beaker, and proceed as above described. After several hours a black deposit will sometimes form at the negative pole of the battery, but it will be found to be readily soluble in chlorhydric acid, and to consist of nothing but iron resulting from the electrolysis of chloride of iron which has passed through the membrane. (Weyl, *Zeitsch. analyt. Chem.*, 1865, **4**, 157).

The Asbestos Filter may be prepared as follows:—Select a not too narrow glass tube, heat a portion of it, near one end, cautiously in the lamp, and slowly draw out the softened and thickened glass in such manner that this part of the tube shall be made much narrower than the rest. Push a loose plug of asbestos down the longer portion of the original tube until it rests upon the beginning of the narrowed portion. Fix the tube in an upright position, and pour into it, upon the asbestos, the substance to be filtered. The asbestos should be thoroughly boiled beforehand with chlorhydric acid to remove soluble impurities, and then ignited in a current of moist air to expel any contamination of fluorine.

Method B. Solution of the iron in sulphate of copper.

Weigh out about 2 grms. of the cast-iron, in the form of borings if it be gray, or of coarse powder if white, place it in a small beaker, pour upon it a solution of 10 grms. of sulphate of copper in 50 c. c. of water, heat the liquid gently and stir it frequently until the whole of the iron has dissolved. Allow the mixture to settle, decant the clear solution and oxidize the moist residue with chromic acid in the manner explained below (Principle II, Method 10). (Ullgren, *Annal. Chem. und Pharm.*, **124**, 59). Or, collect the carbon upon a filter of asbestos, as already explained (A).

Sulphate of copper is preferable to chloride of copper (Method C) since it may be heated without detriment to the analysis. The solution of the iron is consequently far more rapid in this case than when chloride of copper is employed.

Method C. Solution of the iron in chloride of copper. Weigh out about 5 grms. of the finely divided metal, pour upon it a quantity of a concentrated, neutral, or almost neutral, solution of cupric chloride, and let the mixture stand at the ordinary temperature, with occasional stirring, until the whole of the iron has dissolved. The solution of chloride of copper must be as free from acid as possible, and rather more of it must be taken than would be sufficient to convert all the iron into ferrous chloride. The mixture must not be warmed, lest subchloride of copper be formed and a small amount of carburetted hydrogen evolved. (Karsten; Hahn, *Annal. Chem. und Pharm.*, **129**, 76). By pressing the undissolved matter with a glass rod it is easy to determine if any hard lumps of iron are still mixed with it. When the last fragments of iron have dissolved and nothing is left but a crumbly mass of metallic copper, free carbon and the insoluble impurities of the iron, mix the solution with a quantity of chlorhydric acid, together with some more chloride of copper, if this be needed, and wait until the whole of the copper has dissolved to cupreous chloride. Collect the carbon on a tared filter of asbestos (see A) wash it first with water, then with chlorhydric acid to remove subchloride of copper, and afterwards with water to remove the acid. Dry at 120°–130°, weigh and burn to carbonic acid, as in A. The carbonic acid should be made to pass through a small chloride of calcium tube on its way to the soda lime, since the carbon is always contaminated with a small proportion of some hydrogen compound. This method, originally proposed by Berzelius (*Pogg. Ann.*, **46**, 42), is still esteemed. (Compare M. Buchner, *Berg. und Hüttenm. Zeitung*, **24**, 84). According to Ullgren (*Annalen Chem. und Pharm.*, **124**, 59) it yields results somewhat too high, since no allowance is made for the nitrogen in the iron.

Method D. Solution of the iron in chloride of iron. Add to a solution of ferric chloride enough carbonate of calcium to neutralize the free acid,

and pour the filtered liquid upon the iron to be analyzed. The metallic iron will dissolve to ferrous chloride, and a mixture of carbon and other insoluble impurities, together with a quantity of muddy oxide of iron will be left. Dissolve this oxide in chlorhydric acid, and collect and determine the carbon as before. Both C and D succeed best when the iron is finely divided.

In order to pulverize hard cast-iron, beat the metal to moderately small fragments upon an anvil; crush the fragments in a steel mortar and sift the powder in a leaden sieve provided with small apertures. The softer kinds of iron cannot be broken in this way. They must be filed to powder with a sharp file, after the external crust of dirt or oxide has been filed off. — In powdering highly graphitic iron a very considerable loss of carbon may occur. (Booth & Morfit, *Chemical Gazette*, Vol. 11).

Method E. Solution of the iron in acidulated bichromate of potassium.

Dilute a saturated aqueous solution of bichromate of potassium with an equal volume of water and add as much sulphuric acid as will be sufficient to saturate both the potash and the chromic and ferric oxides which are to be formed. By means of platinum pincers or wire, hang a lump of iron (10 or 15 grms.) just beneath the surface of the liquid and leave it at rest. The iron will dissolve rapidly, without evolution of gas, while the carbon remains intact. The hydrogen which may be supposed to result from the action of the acid on the iron is immediately oxidized by the chromic acid before it can become free or combine with any of the carbon. The ferric salt sinks to the bottom of the beaker as fast as it is formed and soon renders the entire liquid opaque. The carbonaceous residue contains a large proportion of iron and appears to be a chemical compound of the two elements. That obtained from steel dissolves completely in chlorhydric acid with violent evolution of hydrogen and carburetted hydrogen. For the method of estimating the carbon in the residue, see A, B and C.

Like Method A, this process dispenses with the trouble of pulverizing the iron. It appears to be specially adapted for the analysis of steel and white iron, since with specular iron a small quantity of hydrogen and carburetted hydrogen is evolved during the process of solution, unless the solution of chromic acid be very concentrated. (Weyl, *Zeitsch. analyt. Chem.*, 1865, 4. 158).

Principle II. Oxidation to carbonic acid, by oxide of copper, chromate of lead, chromic acid, oxygen or air.

Applications. Estimation of carbon in any mixture or compound.

Method I. Combustion with Oxide of copper. (Liebig's method).

The process is well suited for the analysis of

easily combustible, non-volatile, solid or liquid organic compounds. The apparatus required consists of a *combustion tube* of hard Bohemian glass, drawn up to a point at one end, as described in works relating to chemical manipulation; a *combustion furnace*; a light tube full of Chloride of Calcium (*q. v.*) for absorbing water; a set of potash bulbs (see Hydrate of Potassium), and a soda lime tube (see Soda Lime) for carbonic acid; an *air pump* or exhausting syringe, and a small copper dish or porcelain mortar for mixing the substance with oxide of copper; besides corks, and connections of narrow caoutchouc tubing.

The *combustion tube* may be some 40 or 45 c. m. long and should have an internal diameter of 12 or 14 c. m.; the glass of the tube should be about 2 m. m. thick, and of the most infusible quality. Clean the tube from dust by wiping it out with a rag or piece of paper attached to a wooden ramrod or to a blunt wire. The tube will be dried at a later period, as will be explained. Fit to the tube three excellent corks, and carefully perforate two of them, with a fine round file, in such manner that the narrow portion of the chloride of calcium tube, described below, may fit the hole, air tight. Each of the corks should fit the combustion tube so tightly that by pressing strongly with the fingers no more than one third of the cork can be screwed into the tube. The corks should be smooth, soft, and as free as possible from visible pores; they should be dried for a long time at 100°. The purpose of the second perforated cork is to replace the first in case of accident. Instead of ordinary corks, perforated caoutchouc stoppers of good quality may be employed in most cases.

Charge the *potash bulbs* with a clear solution of caustic potash of about 1.27 sp. gr., tolerably free from carbonate. — Caustic soda will not answer so well, since solutions of it are liable to froth. — Wipe the outside of the bulbs with a dry cloth and the insides of the ends of the tubes with slips of twisted filter paper. Close the two ends of the apparatus with little caps formed by plugging short pieces of rubber tubing with bits of glass rod. Hang the bulbs in a room not liable to wide or sudden fluctuations of temperature, and leave them there half an hour or more before weighing.

Fill a bulbed *chloride of calcium tube* with small lumps of the porous chloride, wipe out the narrow portions of the tube, close the two ends of the tube with plugged caps as before, and place it in the room of constant temperature with the potash bulbs.

Fill three quarters of another bulbed tube with granulated *soda lime* and the other quarter with small lumps of porous chloride of calcium, plug the ends of the tube and place it with the others.

Meanwhile put from 0.33 to 0.6 grm. of the substance to be analyzed in a small dry glass

tube, 4 or 5 c. m. long by about 1 c. m. wide, slip the tube into another somewhat larger tube in such manner that it may be closed almost air tight, and weigh the tube and substance. It is well to weigh the empty tubes roughly beforehand in order that a quantity of the substance proper for an analysis may be taken with certainty. The material to be analyzed should be perfectly dry and in the state of fine powder; more or less of it should be taken according as it is supposed to be rich or poor in oxygen.

Weigh the potash bulbs and soda lime tube, and finally the chloride of calcium tube. In case the balance is sensitive when heavily laden, the potash bulbs and soda lime tube may be weighed together. Take care to remove the stoppers of the tubes before weighing and to replace them afterwards.

Fill a Hessian crucible of about 100 c. c. capacity nearly full with soft black oxide of copper, — prepared by igniting nitrate of copper until no more nitrous fumes escape from the mass, — cover the crucible carefully with a tightly fitting cover, heat the crucible with its contents to dull redness in a small fire of charcoal, and set it aside to cool. In case the substance to be analyzed is solid, a porcelain mortar will be needed in which to mix the substance with the oxide of copper. — The mortar should be wide rather than deep, and should have a lip. It should not be glazed inside but must be free from cracks and flaws. Before use, the mortar should be washed clean, dried thoroughly and kept in a warm place until needed. A shallow, oblong copper dish or saucer, provided with a lip at one end, may be employed with advantage for mixing the substance with oxide of copper.

The clean combustion tube should now be thoroughly dried by moving it quickly to and fro over a lamp — so that the entire length of the tube may be heated, — and repeatedly sucking out the hot air from within the tube, through a small, long glass tube which reaches to its bottom.

As soon as the oxide of copper has cooled to such an extent that the crucible which contains it can just be held in the hand, pour a little of it into the porcelain mortar and another small portion into the combustion tube, rinse out both mortar and tube with the warm oxide, and then throw it aside.

Spread a large sheet of glazed paper, such as bookbinders use, upon a clean table, and place the mortar upon it in order that nothing may be lost in case of spilling. Fill nearly two-thirds the length of the combustion tube with the warm oxide of copper, either by repeatedly thrusting the mouth of the tube into the oxide in the crucible held somewhat inclined, and then inverting the tube, or by dipping up the oxide with a tea spoon of German silver and pouring it into the tube through a small, warm copper funnel with a

short neck. — Pour some of the oxide of copper from the combustion tube into the mortar, throw out upon this oxide of copper the substance to be analyzed, from the tube in which it was weighed, taking care to shake the tube so that little or none of the substance shall remain adhering to it. Preserve the empty tube carefully since it must be reweighed. Pour more oxide of copper from the combustion tube to cover the substance in the mortar and mix the substance with the oxide by carefully rubbing the two together with the pestle, taking care not to press upon the latter too strongly. Add to the mixture in the mortar all the oxide of copper in the tube excepting a layer of 3 or 4 c. m. at the very end and incorporate the matter thoroughly. Take out the pestle from the mortar, shake it to remove adhering particles of the mixture, and lay it upon the glazed paper. Carefully transfer the contents of the mortar to the combustion tube by repeatedly thrusting the mouth of the tube into the mixture and then inverting the tube: to transfer the last remnants of the mixture pour them upon a smooth card and thence into the tube. Pour a small quantity of oxide of copper from the crucible into the mortar, rub it about with the pestle so that any particles of the mixture still adhering to the porcelain may be rinsed off, and transfer it to the tube. Repeat this operation of rinsing until the combustion tube is full to within 3 or 4 c. m. of its mouth, then push a not too tight plug of asbestos or of copper turnings against the oxide of copper to keep it in place and close the tube temporarily with a dry cork.

The asbestos should be ignited beforehand in a stream of moist air to remove fluorine, and the copper turnings first in air and then in hydrogen to free them from dirt.

Rap the tube gently against the table until its contents settle together to such an extent that a narrow air-channel is left open above the oxide of copper from one end of the tube to the other, for the passage of the gases which are to be evolved, and that the upturned posterior point of the tube is left clear. Carry the tube to an air pump or simple exhausting syringe to which is attached a long tube full of dry chloride of calcium, and connect the combustion tube with the latter, by means of a perforated cork. Place the combustion tube in a narrow wooden box or trough, fill the box with hot sand so that the entire length of the tube shall be covered with the sand and then slowly pump out the air which is contained in the tube. The sand must not be hot enough to singe paper. The pumping must be careful and deliberate or some of the contents of the combustion tube will be carried out with the escaping air. After a moment slowly open the stop-cock of the pump so that fresh air may enter the combustion tube. All the moisture contained in this fresh air will be stopped by the chloride of calcium, as well as that brought

out of the tube in the exhausted air. Again carefully pump out air from the tube, then admit more air and continue to exhaust and to admit air alternately some 10 or 12 times in order to remove the last traces of moisture which may have been absorbed by the oxide of copper during the operation of mixing.

Instead of operating as above described, a better way is to place the combustion tube upright in a retort holder, to mix the substance with oxide of copper in a small copper dish, and to pour the mixture into the tube through a smooth, warm copper funnel. The anterior portion of the tube may then be filled with a tightly packed layer, 20 c. m. long, of hard, gray, granulated oxide of copper, which, unlike the soft oxide above described, has but little power of absorbing moisture from the air. (Mulder). By proceeding in this way the necessity of pumping may be done away with.

Bunsen's Modification. Another way of avoiding the moisture of the air and of dispensing with the need of an air-pump has been indicated by Bunsen. This chemist directs that the substance to be analyzed be thrown directly into the combustion tube and there mixed with oxide of copper by means of a twisted wire, instead of being rubbed with the oxide in a mortar or other dish. His process is particularly well adapted for the analysis of highly hygroscopic bodies and of substances which would be decomposed by warm oxide of copper.

The hot oxide of copper is transferred from the crucible in which it was ignited to a warm, dry glass flask, or wide tube closed at one end, which is then corked tightly and left to cool. The substance to be analyzed is meanwhile weighed in a long tube of thin glass provided with a cap cover, as described above. This weighing tube should be about 20 c. m. long and 6 or 7 m. m. wide. — As soon as the oxide of copper has become cold, uncork the flask or tube which contains it, thrust the end of the dry combustion tube through the neck of the flask into the oxide of copper, in such manner that a small quantity of the oxide may enter the tube; rinse the combustion tube with this oxide and throw the rinsings aside. Again thrust the combustion tube through the neck of the flask into the oxide of copper and take up enough of the latter to form a column or layer about 10 c. m. deep at the posterior end of the tube. — The transfer of oxide from the flask to the tube is readily effected by holding the tube in a slightly inclined position and gently tapping the tube. — Open the weighing tube, thrust it as far as possible into the combustion tube, held slightly inclined, and pour out the substance to be analyzed. In doing this, turn the weighing tube about so that its contents may fall out more readily, and at the same time press its rim against the upper side of the combustion tube in order to keep it

from touching the substance after it has once fallen out. As soon as the substance to be analyzed has been poured from the weighing tube, bring the combustion tube into a horizontal position so that the weighing tube, still pressed against its upper side, shall be slightly inclined, with the closed end downwards. Then slowly withdraw the weighing tube, taking care to turn it so that any portions of the substance which may have remained attached to the rim of the tube may fall back into it. Close the empty tube and put it aside to be weighed. — Transfer from the filling flask to the combustion tube another quantity of oxide of copper equal to the first, so that there shall be a column of oxide of copper 20 c. m. long at the end of the tube, with the substance in the middle of it. To mix the substance with the oxide of copper, provide a long, bright, stiff iron wire, bent to a ring or loop at one end, for the handle, and at the other end pointed and twisted like a cork screw, with a single twist. Push the screw end of the wire deep into the oxide of copper and move it about rapidly for a few minutes in all directions, so that the substance and oxide may be intimately mixed. Withdraw the wire, transfer a new quantity of oxide of copper from the filling flask to the tube, wipe the wire in this oxide, and finally fill the tube with oxide of copper. — So little water is absorbed by the oxide of copper in this process that a single charge of the filling flask may be made to serve for several analyses. If the flask be provided with a tight cork the oxide of copper will remain several days fit for use, even though the flask be repeatedly opened and portions of its contents withdrawn. (Bunsen, *Handwörterbuch der Chemie*, Supplement, p. 186).

As soon as the combustion tube has been properly filled, and freed from hygroscopic moisture, thrust the narrow end of the weighed chloride of calcium tube through one of the dry perforated corks, twist the cork tightly into the mouth of the combustion tube, and place the latter in a "combustion furnace." The combustion furnace may be fed with charcoal, alcohol, or far better, with gas, in accordance with almost any one of the numerous plans described by works on chemical manipulation. Compare, for example, Baunhauer (*Annal. Chem. und Pharm.*, 90. 21), J. Lehmann (*ibid.*, 102. 180), Heintz (*Pogg. Ann.*, 103, 142), Hofmann (*Journal Chem. Soc.*, 11. 30).

Copper foil for wrapping soft tubes. In case the combustion tube has to be made of glass which is not infusible enough to withstand the heat of the furnace, the tube should be wrapped in thin copper foil or gauze, and wound around with iron wire, before it is placed in the furnace. Or the tube may be laid in a shallow trough of sheet iron.

The combustion tube should incline forward slightly, and its mouth should project at least

an inch beyond the edge of the furnace, and a screen of sheet iron should be placed at the edge of the furnace so as to protect the mouth of the tube from excessive heat. Throughout the experiment the projecting part of the tube should be kept so hot that the fingers can hardly bear the shortest contact with it; but no hotter than this, lest a portion of the cork be burned, and the analysis thereby vitiated.

By means of a short rubber connector, attach the potash bulbs to the free end of the chloride of calcium tube, taking care to place the largest bulb next to the chloride of calcium tube, and tie the ends of the connectors firmly to the glass with fine cords. During the operation of tightening and tying the cords, the ends of the two thumbs should be pressed firmly together, so that no part of the apparatus need be broken in case a cord happens to give way. It is well, also, to rest the fragile bulbs upon a folded cloth, or some other soft substance. To the free end of the potash bulbs attach, with another connector, the supplementary soda lime tube, and support it in a horizontal position by means of a ring-stand, or any other suitable prop.

In order to determine whether the fittings of the apparatus are air-tight, hold a tolerably large piece of glowing charcoal near the largest potash bulb, so that the air within the bulb may be expanded, and in part driven out of the apparatus. After a certain amount of air has been expelled in this way, take away the coal. Note the height to which the potash solution rises in the large bulb to replace the lost air, and observe whether the liquid remains at this height for the space of three or four minutes. If the apparatus be tight, the liquid will remain at the highest level to which it rose as the bulb cooled; hence, if it gradually recedes from the large bulb, and comes to a common level in both limbs of the apparatus, either one of the corks or connectors must be leaky, or the apparatus somewhere cracked.

The weight of the empty weighing tube may be conveniently taken while the tightness of the tube is being tested.

Heating the tube. After the apparatus has been proved to be tight, heat carefully two or three inches of the anterior portion of the combustion tube until it is red hot, then slowly work backwards inch by inch, taking care to bring each section of the tube to redness before proceeding to heat the next section. If charcoal be used as the fuel, the unheated portion of the tube must be protected from the radiant heat of the fire by means of a sheet-iron screen, which may be moved backwards at will with a pair of tongs or pincers.

When heat is first applied to the tube, some bubbles of air will be driven through the potash bulbs by virtue of simple expansion; afterwards, when the heat reaches that portion of the oxide of copper which was used to rinse

the mixing mortar, or to wipe the mixing wire, and carbonic acid begins to be evolved, the rest of the air in the apparatus will escape in large bubbles. But when the actual mixture is reached, the bubbles which pass into the potash are nearly pure carbonic acid, so that only now and then a solitary air bubble will escape through the liquid. — The heating of the tube should be so regulated that the gas bubbles may follow one another at intervals of from one-half to one second.

After about three quarters of an hour, when no more gas is evolved, although the tube is red hot from end to end, take away the fire from the posterior end of the tube, so that the upturned point may be free, and place a screen between the point and the fire. The cooling of the end of the tube thus caused, taken in connection with the absorption of carbonic acid by the potash lye, will cause the latter to be forced back into the large bulb. The liquid will rise slowly at first, but with increased rapidity after it has once entered the large bulb, but there is no danger of its flowing into the chloride of calcium tube if the bulbs were properly filled in the first place, and are now set level. It may here be said, that during the combustion it is well enough to place a cork, or a piece of wood as thick as a man's finger, beneath that end of the potash bulbs (Liebig's bulbs) which is farthest from the large bulb, so that the liquid shall tend to flow into the large bulb. But as soon as gas bubbles cease to come forward, this prop must be removed, and the bulbs brought to a level position. — At the moment when the large bulb has become about half full of the potash lye, crush the end of the upturned point of the combustion tube with a pair of stout pincers, and push over the stump a dry glass tube about 60 c. m. long, and open at both ends. Support this tube in an upright position by means of a ring-stand. Attach a long caoutchouc tube to the supplementary soda-lime tube beyond the potash bulbs, bring the potash bulbs to their original oblique position, and with the mouth, or better with a small aspirator, suck air through the combustion tube until the bubbles which pass through the potash bulbs cease to diminish in size. An aspirator has an advantage in that it affords ocular evidence of the volume of air which is drawn through the apparatus.

Take the apparatus to pieces, stop the ends of the chloride of calcium tubes and of the potash bulbs with rubber connectors plugged with glass, set the larger chloride of calcium tube in a vertical position, with its bulb upward, and leave the several pieces in the room of constant temperature for half an hour before weighing. The increased weight of the larger chloride of calcium tube gives the amount of water produced in the combustion, and from this weight that of the hydrogen in

the substance analyzed is obtained by the following proportion:—

Molecular wt. of H_2O : Wt. of an atom of H : Wt. of water found : x ($=$ Wt of H in substance taken.)

The increased weight of the potash bulbs and supplementary soda lime tube gives the weight of the carbonic acid, whence the weight of carbon is derived by the proportion:—

Molecular wt. of CO_2 : Weight of an atom of C : Wt. of CO_2 found : x ($=$ Weight of C in the sample.)

In practised hands, this comparatively old process gives excellent results. It is, however, far less convenient and trustworthy than the process of combustion with oxide of copper in a current of oxygen gas (see below, Method 2), and is therefore seldom employed. — In operating with easily combustible substances (and the process is really only suitable for the analysis of such), it is easy to determine in this way the proportion of carbon with great accuracy, but as regards hydrogen, the results obtained are usually about 0.1 or 0.15 per cent higher than the truth. This excess of hydrogen comes in part from moisture absorbed by the oxide of copper, but mainly from the moisture of the air, which is drawn through the apparatus at the close of the combustion to remove the carbonic acid. The error can be corrected in good part by attaching, with a perforated cork or rubber connector, a tube full of solid hydrate of potassium to the posterior point of the combustion tube,—in place of the upright open tube above described,—before beginning to suck air through the tube.

Volatile substances, and those liable to lose water, or to undergo other alteration at 100°, may be analyzed in this way, though less readily than by Method 2, by mixing them with cold oxide of copper, in the manner proposed by Bunsen, see above, p. 61.

Volatile liquids, such as alcohol, ether, essential oils, and the like, had better be analyzed by Method 2 or 6. In case they are analyzed by Method 1, the combustion tube should be 50 or 60 c. m. long, the oxide of copper should be cooled in a flask (p. 61), and the liquid weighed in two or three small bulbs similar to those described under Method 2 only smaller. — Pour a layer of the cold oxide of copper, 6 c. m. deep, into the combustion tube, scratch the stem of one of the bulbs with a file or steel glass-knife, break off the point quickly with the thumb and finger, and drop both bulb and point into the combustion tube. Pour another layer of oxide of copper, 6 or 8 c. m. deep, into the tube to cover the bulb, throw in the second bulb in the same way as the first, and add another layer of oxide of copper. If the substance to be analyzed contains a large proportion of carbon, and is rather difficultly volatile, the quantity (about 0.4 grm.) taken for analysis, had better be weighed in three than in two bulbs, in order that no particles of carbon may

be left unconsumed with the mass of reduced copper. Rap the tube gently against the table to clear a passage for the gases which are to be evolved, and finally fill the anterior half of the tube with small lumps of hard oxide of copper, or with copper turnings which have been superficially oxidized, so that there may be free passage for gases and vapors, although little or no visible channel is left open above the mass. — After the chloride of calcium tube, potash bulbs, etc., have been attached to the combustion tube, place a screen at the middle of the tube and heat the anterior column of oxide of copper to redness. Heat the upturned, posterior point of the tube so that no vapor shall condense in it, and place a hot coal, or an exceedingly small flame, near that part of the tube which contains one of the bulbs. The contents of the bulb should be driven out very slowly, and the whole operation conducted with extreme care. It is an easy matter to lose an analysis by distilling the substance rapidly, so that considerable quantities of partially burned material can escape through the potash bulbs. — After the contents of the first weighed bulb have been driven out and consumed, that part of the tube which contains the second bulb may be heated. The combustion tube is finally heated from end to end, and the analysis finished in the usual way. — In the case of liquids which are but slightly volatile, it is well to empty the bulbs before the combustion begins, instead of heating them, as above described. To this end attach the filled combustion tube to an air pump, and give a single slow stroke with the pump handle. The bubbles of air within the weighing bulbs will expand, and the liquid be forced out to be absorbed by the oxide of copper. Bodies rich in carbon should never be analyzed in this way; a supply of oxygen gas is needed in order that their carbon may be completely consumed. See Methods 2 and 6.

Nonvolatile Liquids are analyzed by Methods 2, 3, 5 and 6.

Nitrogenous Compounds. When substances containing nitrogen are ignited with oxide of copper, most of the nitrogen goes forward in the gaseous form, together with the carbonic acid and water, and escapes into the air as free nitrogen. A small quantity of the nitrogen, however, is converted into nitric oxide, and the latter, on coming in contact with the potash lye, is partially decomposed to nitrous acid, which combines with the potash. A part of the nitric oxide changes into hyponitric acid also, by coming in contact with the air in the apparatus, and the acid thus formed is absorbed, as well as the carbonic acid, in the potash bulbs. Though the amount of nitrous and nitric acids thus generated is never very large, there is still enough formed in many cases, especially in the combustion of substances rich in oxygen, to vitiate the determination of carbon. The difficulty may be ob-

viated in some cases by mixing the substance very intimately with the oxide of copper, and conducting the combustion very slowly. But as a general rule, the oxides of nitrogen must be decomposed by bringing them in contact with red hot metallic copper. The metal is used either in the form of turnings, or of rolls or spirals, made of wire or of strips of sheet copper. The rolls or spirals may be 8 or 10 c. m. long, and just thick enough to be admitted to the combustion tube. If turnings are used, they may be compressed to a cylindrical form, by forcing them while hot into a short tube, a little narrower than that in which the combustion is to be made. According to Schroetter and Lautemann (*Jour. prakt. Chem.*, 77. 316), the copper rolls or turnings cannot be replaced by the metallic powder obtained by reducing oxide of copper with hydrogen, since the powder obstinately retains hydrogen, which, by reacting upon carbonic acid in the process of the combustion, causes an appreciable quantity of carbon to be lost as carbonic oxide. — The rolls or plugs of copper are first heated to redness in the air in a Hessian crucible, until the surface of the metal is oxidized, and the last trace of dust and oil has been burned off; they are then heated in a tube in a stream of hydrogen, until the oxide has all been reduced. Since recently reduced copper retains hydrogen gas, and on exposure to the air absorbs aqueous vapor, it should always be heated to 100° in the air for some time before it is used, and should be as nearly as possible at this temperature when introduced into the combustion tube. — The combustion tube, which should be 12 or 15 c. m. longer than if it were to be employed for analyzing a body free from nitrogen, is filled in the usual way, with this exception, that enough metallic copper is placed at the anterior end, to form a column 10 or 12 c. m. long. As soon as the tube is laid in the furnace, the metallic copper is heated to bright redness before proceeding to the ordinary steps of the analysis. Hot copper decomposes all the oxides of nitrogen, fixing the oxygen while nitrogen goes free; but since this action occurs only when the metal is intensely ignited, care must be taken to keep the metal hot throughout the entire combustion. Compare the heading, Nitrogenous Compounds, under Method 2.

Sulphur Compounds. In determining the carbon of compounds which contain sulphur as well as carbon, hydrogen, oxygen or nitrogen, it has hitherto been customary to proceed, as above described, as if nothing but carbon, hydrogen and oxygen (or nitrogen) were present, but to place between the chloride of calcium tube and the potash bulbs a narrow tube, 10 or 12 c. m. long, filled with dry binoxide of lead, in order to absorb the sulphurous acid formed by the oxidation of the sulphur, which would otherwise be absorbed in the potash

bulbs. (Liebig & Wöhler). But according to Carius (*Annal. Chem. und Pharm.*, 116. 28), all the sulphurous acid cannot be retained in this way when the substance analyzed contains a large proportion of sulphur, and on the other hand, Bunsen has shown that binoxide of lead is capable of absorbing no inconsiderable quantity of carbonic acid. Carius urges that sulphur compounds had better be burned with chromate of lead. (See Method 8). See also Sulphur.

Chlorine, Bromine and Iodine Compounds. When organic substances containing chlorine, bromine or iodine are burned with oxide of copper, subchloride (bromide or iodide) of copper is formed, some of which is liable to condense in the chloride of calcium tube and vitiate the determination of the hydrogen. Hence the compounds in question are usually burned not with oxide of copper, but with chromate of lead (Method 8). Compare Method 2.

In Analyzing Compounds which contain Inorganic Constituents, other than those allowed for in the preceding paragraphs, the proportion of inorganic matter must be determined in a special portion of the material. The analysis of such compounds presents no particular difficulty unless a volatile metal like mercury or a metal capable of retaining more or less carbonic acid, — such as potassium, sodium, calcium, strontium or barium, be present. In the combustion of substances which contain mercury, a layer of copper turnings (see Nitrogenous substances, above) may be placed in the anterior part of the combustion tube in order to retain the metal within the tube. Care must be taken not to heat this copper too strongly. If the substance to be analyzed contains metals capable of retaining carbonic acid, a quantity of some substance capable of decomposing the carbonates in question at high temperature may be added to the oxide of copper with which the substance is mixed; either teroxide of antimony, phosphate of copper or boracic acid, will answer the purpose. See also Method 9, and the remarks on same subject under Method 2.

Method 2. Combustion with oxide of copper, in conjunction with oxygen gas forced from a gas-holder.

In this process the substance to be analyzed, or at least the volatile products given off from it by distillation, is heated in contact with oxide of copper in the midst of a slow current of oxygen gas which is made to flow in continually upon the mixture from a gas-holder. The method, besides being suitable for the analysis of difficultly combustible substances, is of general applicability for the estimation of carbon and hydrogen in all organic substances. It will be found particularly convenient when several analyses are to be made in succession, and in cases where from our inability to pul-

verize the substance to be analyzed it cannot be intimately mixed with oxide of copper or any other solid oxidizing agent.

Besides the apparatus described under Method 1, the process now in question requires a couple of gas-holders and a permanent set of drying tubes. For a simple and inexpensive form of gas-holder, see Eliot & Storer's *Manual of Inorganic Chemistry*, Appendix § 11, Fig. xvii.

Provide a straight combustion tube open at both ends, about 60 c. m. long, and of any width to which corks can be conveniently fitted. Fit sound corks to both ends of the tube. Perforate the corks so that one of them may fit the weighed chloride of calcium tube, and the other a short, straight tube of diameter proper to be connected with the permanent drying tubes; then dry the corks at 100°.

Place a tolerable compact plug of clean copper turnings or a loose plug of asbestos (previously ignited in a current of moist air in order to remove fluorine) in the combustion tube at a distance of 4 or 5 c. m. from its anterior end, pour enough oxide of copper into the tube to fill two-thirds of it, and push down upon the oxide of copper another loose plug of asbestos to keep the column in place. A space about 20 c. m. long should be left open at the posterior end of the tube. The oxide of copper had better be in the form of coarse granules free from dust; it need not be dried or ignited before being placed in the tube. Or, instead of mere oxide of copper, the tube may be charged with a mixture of asbestos and fine oxide of copper. When mixed with asbestos, the oxide of copper in the tube will be light as well as porous, and the tube will better preserve its shape when heated.

Lay the tube in a shallow trough or gutter of sheet iron, upon a thin layer of calcined magnesia or of asbestos, and place the gutter and tube in the combustion furnace.

Unless the glass of the combustion tube is of the most refractory character the tube had better be coated with clay or with asbestos, and then covered with copper foil bound round with copper or iron wire, before it is placed in the furnace. The furnace may be heated with alcohol or with charcoal, in default of gas.

The posterior end of the combustion tube is in the next place connected with the *Permanent drying (or rather, cleaning) tubes*.

These tubes, which serve to purify air and oxygen for the analysis, stand between the combustion tube and the gas-holders which supply air and oxygen; they may consist of a set of large potash bulbs filled with oil of vitriol, a large U-tube full of soda-lime, and another U-tube filled with chloride of calcium. The sulphuric acid bulbs are attached to the gas-holder, while the chloride of calcium tube is connected with the posterior end of the combustion tube. Where many analyses are to be made, it is well to have two or three soda-lime tubes and as many more charged with chloride

of calcium. In order that a single set of the tubes may serve for both gas-holders without inconvenience, a supplementary flask may be attached to the set, as follows:—Fit to a small, wide mouthed flask a caoutchouc stopper, with three perforations. Provide three glass tubes suited to the stopper and each bent at a right angle. One of the tubes is a simple abduction tube only long enough to pass through the stopper, while the other two must be long enough to reach almost to the bottom of the flask. Fill the flask one-third full of strong potash lye, place it between the gas-holders and the sulphuric acid bulbs and attach it to the latter by means of a rubber connector, tied to the short abduction tube. To the other end of each of the longer tubes tie a piece of thick caoutchouc tubing about 3 inches long, close each of these rubber connectors with a spring clip, and by means of glass tubes attach one of them to the opening of the gas-holder which contains air and the other to the oxygen-holder. By opening one or the other of the clips, air or oxygen may be made to flow into the combustion tube at will, and by renewing from time to time the potash lye and the sulphuric acid in the flask and bulbs the efficiency of the apparatus may be kept up for a long time. (Piria, *Kopp & Will's Jahresbericht*, 1857, p. 573).

As soon as the combustion tube has been laid in the furnace, start a slow current of air through the tube and heat it throughout its entire length, at first very gently but afterwards to low redness, in order to dry the oxide of copper. During this preliminary ignition leave the anterior end of the tube open, but as soon as the tube has been thoroughly heated close it with a dry cork carrying an unweighed chloride of calcium tube, extinguish the fire, and without interrupting the slow current of air, allow the tube to cool.

Weigh out the substance to be analyzed, in a small boat of platinum, copper, porcelain or glass, inclosed in a glass weighing tube which has been weighed together with the boat before the introduction of the substance. Push the loaded boat into the posterior end of the combustion tube until it almost touches the asbestos plug, replace the cork at the end of the combustion tube and for the time being shut off the current of air. It is well to lay two or three fibres of asbestos beneath the boat to prevent it from fusing to the glass. From 0.3 to 0.5 gm. of substance should be taken as a general rule, though less of the substance will be needed in proportion as it contains more carbon; 0.2 of a gm. of material is sufficient for the analysis of many hydrocarbons.

After the boat has been introduced, remove the unweighed chloride of calcium tube from the anterior end of the combustion tube, replace it with the weighed chloride of calcium tube and attach to the latter the weighed potash bulbs and the soda-lime tube as described under Method 1 (see p. 62).

In order to determine whether the apparatus is tight, open the cock of the oxygen gas-holder slightly so that a very slow current of the gas may pass through the tube, and after a moment suddenly close it again. Then watch the level of the liquid in the potash bulbs. If the liquid does not sink back from the outermost bulb in the course of a few minutes the apparatus is tight enough for use. In applying this test the tube must of course be as cold as the surrounding air. — Place a sheet iron screen across the end of the tube to protect the cork from the fire and proceed to heat the oxide of copper in the tube, with the exception of a couple of inches next the substance to be analyzed, and as soon as it has become red hot start a slow current of oxygen through the tube. Then slowly heat the rest of the oxide of copper, and finally the substance itself, with extreme care. The substance must neither be heated too quickly nor the stream of oxygen made too strong. It is to be remembered, however, that an amply supply of oxygen will be most needed at the moment when the substance is distilling most rapidly. There is no harm in using so much oxygen that an excess of it shall slowly bubble through the potash bulbs from first to last. In order that the current of oxygen may be readily controlled and nicely adjusted the cock of the oxygen gas-holder should be provided with a long lever.

When the substance to be analyzed has been completely burned, and the character of the bubbles in the potash apparatus indicates that no more carbonic acid is coming forward, shut off the oxygen, turn on air, and allow the apparatus to cool in a slow stream of air. Since oxygen is heavier than air it is important to expel it thoroughly from the potash bulbs. Enough air will have been passed through the tube when a glowing splinter of wood ceases either to burst into flame or to glow vividly when held in the air which issues from the weighed soda-lime tube. — As soon as all the oxygen has been forced out of the apparatus, remove the chloride of calcium tube, the soda-lime tube and the potash bulbs to the room of constant temperature, and after half an hour weigh them as directed in Method 1 (p. 62). Withdraw the boat from the combustion tube and weigh the ashes contained in it, if any there be. Unless some accident occur, the combustion tube and oxide of copper are left in perfect order for a new analysis. The operator has only to push another boat charged with a new quantity of substance into the tube and to attach another set of weighed chloride of calcium tubes, etc., to the anterior end of the tube.

To guard against the possibility of the escape of any of the products of distillation backwards to the cork and drying tubes, Piria, (*Kopp & Will's Jahresbericht*, 1857, p. 573) interposes hot oxide of copper between the substance to be analyzed and the posterior end of

the tube, as follows: — The anterior portion of a tube 80–85 c. m. long is filled with granulated oxide of copper, as above described, the boat loaded with the substance is pushed in nearly to the oxide of copper and a couple of coils of superficially oxidized copper foil are thrust in behind the boat. The tube and oxide of copper are dried in a current of air in the usual way, but in making the combustion the posterior portion of the tube is heated to redness, as well as the anterior portion, before the substance to be analyzed is warmed. Screens are employed to protect that portion of the tube which contains the substance, while the rest of the tube is being heated.

Instead of placing the substance to be analyzed in a boat, as above described, it may be mixed directly with a part of the oxide of copper in the tube. To this end, weigh the substance in a long, narrow, weighing tube (see p. 61), and pour it upon the posterior end of the column of oxide of copper (see p. 65) after the latter has been dried in a current of air in the usual way, and allowed to become cold. Mix the substance with the oxide of copper by means of a twisted iron wire, such as has been described on p. 61, and then fill the tube to within about 12 c. m. of its end with coarse oxide of copper, which has previously been ignited, and cooled in a corked flask (see p. 61). Tap the tube gently against the table to shake down the oxide of copper, so that a narrow passage may be left above it. Replace the tube in the furnace, and connect its posterior end with the permanent drying tubes, and attach to it the weighed chloride of calcium tube, potash bulbs, etc. Start a very slow current of oxygen through the tube and proceed to heat first the anterior column of oxide of copper, then the mixture, and finally the posterior column of oxide,—working backwards always from the front end of the tube. Take care to protect both the corks with sheet-iron screens. A moveable screen will be found useful, also, for regulating the heat at that part of the tube which contains the mixture. Throughout the analysis cause a slow current of oxygen to pass through the tube. The stream should be so slow, however, that no oxygen shall escape through the potash bulbs while the substance is actually burning. After the evolution of carbonic acid has ceased, force a more rapid current of oxygen into the tube until the reduced oxide of copper has been completely revived, and finally throw in a current of air to sweep out the excess of oxygen. As a general rule, however, it will be found more convenient and satisfactory to make use of a boat instead of mixing the substance with oxide of copper. When boats are employed, the same combustion tube may not only be used over and over again for many analyses, but needs absolutely no preparation after one analysis, to fit it for the next.

Liquid Substances. In case the substance to

be analyzed is liquid, but not readily volatile, such, for example, as a fatty oil, it may be placed in the combustion tube in a boat, as described. Wax, and other easily fusible matters, may be melted and allowed to cool in the boat before weighing. The combustion tube had better be rather long, and provided with a posterior column of oxide of copper (compare Piria, above). When the oxide of copper has been heated to redness at both ends of the tube, place a piece of red hot charcoal near the boat, so that the substance may be slowly distilled. Increase or diminish the heat at the boat, and at the same time regulate the stream of oxygen in such manner that the copper reduced by the products of distillation may be oxidized as fast as it is formed. At the close of the combustion take care to burn off all the carbon from the boat.

In analyzing substances, such as some of the heavier components of petroleum, which volatilize only at temperatures so high that their vapor would ignite as soon as formed, and explode in the atmosphere of oxygen which fills the tube, a cap or cover of asbestos fibres, roughly woven, attached to a stiff wire, may be placed over the boat after it has been pushed into the tube. The asbestos cloth acts as a safety screen to prevent explosions, like the wire gauze of Davy's lamp. (Peckham).

Volatile Liquids. For the analysis of liquids which volatilize at comparatively low temperatures, select a stick of combustion tubing 50 or 60 c. m. long, and bend it slightly, at a distance of about 12 c. m. from one end, so that the posterior end of the tube may point upwards, and the lower edge of the extremity of the tube reach to a height of 8 or 9 c. m. above the level of the sheet-iron trough in which the horizontal part of the tube reposes. Pack the horizontal portion of the tube either with a mixture of oxide of copper and asbestos, or with coarse oxide of copper, secured with asbestos plugs, and dry the tube in the furnace with a current of air, in the usual way.

In order to introduce the substance into the tube, blow a couple of light weighing bulbs, about a centimetre in diameter (not too large to slip readily into the combustion tube), with capillary stems 5 or 6 c. m. long. Weigh the empty bulbs one at a time, and place them in paper trays bearing descriptive marks or numbers. Pour some of the liquid to be analyzed into a porcelain crucible or small dish—kept cool with ice, if need be—warm each bulb in succession at a lamp, and as soon as the glass is hot thrust its stem into the liquid in the dish. As the glass cools, the liquid will rise up into the bulb and fill it more or less completely. In case the liquid is highly volatile, a portion of that which first enters the partially cooled bulb will be converted into vapor, so that, for the moment, the rest of the liquid will be driven out; but as soon as the vapor in the bulb condenses, a new portion of

the liquid will rise into the bulb and fill it more completely than before. With less volatile liquids, only a small quantity of the fluid will enter the bulb at first, but it is easy to fill the bulb completely by heating the liquid which first enters until part of it is converted into vapor, and again thrusting the stem into the liquid. To throw out any excess of liquid which may remain in the stem, suddenly jerk the bulb; then hold the point of the stem in a fine blowpipe jet until the glass fuses, and the bulb is closed. Weigh each of the bulbs with its contents. Each bulb should contain from 0.3 to 0.4 grm.—enough for a single analysis. The duplicate bulb will replace the first in case of accident.

After the combustion tube has been dried, cooled, connected with the weighed chloride of calcium tube, potash bulbs, etc., and proved to be tight, take out the posterior cork of the combustion tube and make a slight scratch upon the stem of one of the bulbs full of substance, by means of a sharp file, or a knife of hard steel, proper for scratching glass. This file-mark should be near the point of the stem. Place the stem of the bulb within the combustion tube, and press its point firmly against the side of the tube until it breaks at the file mark. The moment the stem breaks, drop the bulb, point downwards, into the tube, replace the cork, put a screen in front of the substance, 9 or 10 c. m. from the bend in the tube, heat the anterior column of oxide of copper, and start a slow current of oxygen through the tube. When the copper has become hot remove the screen, or set it backwards towards the substance, accordingly as the latter is more or less volatile, and finally heat the substance itself carefully with a hot coal, or better, with a thick rod of copper. The copper bar may be laid across the ring of a lamp stand, in such manner that while one end of the bar can be brought close to the combustion tube, above the substance to be analyzed, the other end can be heated to redness by means of a Bunsen's lamp. By moving the lamp-stand to and fro, so that more or less of the hot copper is brought near the bulb, the distillation of the substance may, in most instances, be easily controlled. (Warren).

Great care must always be exercised in heating the bulb in order that its contents may not distil too rapidly. Unless due attention be paid to this particular the combustion of the substance is liable to be incomplete, and gaseous carbon compounds will pass off unabsorbed through the potash bulbs. Sudden heating of the substance would, in many cases, occasion a rush of gas strong enough to throw some of the potash lye out of its bulbs, and to project vapors backwards into the permanent drying tubes. — In order to avoid explosions, it is essential that the empty, inclined portion of the combustion tube shall never be heated to a temperature high enough to ignite the vapor of

the substance, until after the last portions of this vapor have been swept forward by the current of oxygen. Throughout the analysis the supply of oxygen gas must be sufficient to re-oxidize the copper almost or quite as fast as it is reduced.

To prevent any portion of the vapor of the substance from being lost at the posterior end of the tube, it is well to admit the oxygen through a special tube of hard glass loosely packed with asbestos and kept hot during the combustion by means of a Bunsen's lamp. This tube is placed between the combustion tube and the permanent drying apparatus and is attached to the latter by means of a perforated cork; at the anterior end, which enters the combustion tube, it is drawn out to a short, blunt point, having an opening no larger than will admit a small needle. The oxygen is thus made to enter the combustion tube in a rapid stream, against which little or no vapor can pass back. The hot oxygen, moreover, prevents the condensation of any vapor near or upon the cork. (Warren).

Hygroscopic Substances. Compounds which absorb water so rapidly from the air that they cannot be readily dried and weighed in the ordinary way may be dried in the combustion tube, as follows:—Pack the combustion tube with oxide of copper, as above described, lay the tube in the furnace upon a sheet-iron gutter so short that it does not reach behind the column of oxide of copper, dry the tube and oxide in the usual way and attach to it the weighed chloride of calcium tube. Weigh out the air-dried substance in a boat and push the boat into the combustion tube as far as the oxide of copper. Heat the empty, posterior part of the tube, at a distance of 3 or 4 inches from the boat, and pass a slow current of dry air through the tube. At the same time heat the column of oxide of copper gently so that no water can be deposited in the anterior part of the tube. Keep up the stream of hot air as long as any water is seen to be deposited in the neck of the chloride of calcium tube, then allow the combustion tube to cool, without checking the current of air, and re-weigh the chloride of calcium tube. Subtract the weight of the water thus found from the weight of the substance taken, in order to obtain the weight of really dry material to be analyzed. Replace the chloride of calcium tube, attach the potash bulbs and the soda lime tube and proceed with the analysis.

In a similar way, the water of crystallization of many substances may be determined:—To this end suspend a sheet of copper-foil beneath the combustion tube, between the substance and the source of heat, place the bulb of a thermometer above the foil and light the fuel beneath the foil; heat the tube to the temperature necessary to expel the water from the substance. In case the substance to be dried is liable to decomposition, the weighed chloride of

calcium tube should be connected with a set of weighed potash bulbs. By re-weighing the latter after the substance has been dried, it is easy to determine whether any carbonic acid has been produced. (W. Stein, *Journ. prakt. Chem.*, 100. 55).

Nitrogenous Compounds. In case the substance to be analyzed contains nitrogen, choose a combustion tube about 80 c. m. long, pack it at the anterior end with clean copper turnings to a depth of 15 or 18 c. m. (Compare the heading Nitrogenous Compounds under Method 1), fill in with oxide of copper in the usual way and proceed with the analysis. Take care to regulate the streams of air and oxygen so that the anterior half at least of the column of copper turnings shall not be oxidized either in the process of drying or during the actual combustion. The stream of oxygen must be very slow. When the combustion of the substance is complete and it is seen that the copper turnings are rapidly oxidizing, shut off the oxygen and let the tube cool in a slow current of air.

According to Stein & Calberla (*Journ. prakt. Chem.*, 104. 232) silver turnings may be used with advantage, instead of copper, for reducing oxides of nitrogen, — as well as for retaining chlorine, as described below. Red-hot silver decomposes nitric oxide completely but has no action upon carbonic acid.

Sulphur Compounds. See this heading, under Method 4.

Chlorine, Bromine and Iodine Compounds. When chlorine, bromine or iodine compounds are burned with oxide of copper in conjunction with oxygen gas, there is not only danger of some dichloride (bromide or iodide) of copper being carried forward into the chloride of calcium tube, as has been already explained (Method 1, p. 64), but some of the dichloride is always decomposed by the oxygen gas into oxide of copper and free chlorine. Part of the chlorine thus evolved is retained in the chloride of calcium tube and part of it is absorbed by the potash lye. Though the error from this source is usually small, it must always be carefully guarded against by placing a column of metallic copper in the front part of the tube (see Nitrogenous compounds, above) and keeping the metal red hot throughout the combustion. At the close of the analysis the current of oxygen should be arrested as soon as the copper begins to oxidize lest the chloride of copper which has formed upon it be again decomposed. (Staedeler, *Annalen Chem. und Pharm.*, 69. 334).

According to Kraut (*Zeitsch. analyt. Chem.*, 1863, 2. 242) it is best to push back the column of metallic copper about 5 inches from the mouth of the tube, and to place a roll of silver foil in front of the copper. If this be done the stream of oxygen may be kept up as long as may seem fit, at the close of the operation, without any risk of chlorine being carried

forward into the potash bulbs. The silver is of use also, inasmuch as, unlike the copper, it prevents any dichloride (bromide or iodide) of copper from passing into the chloride of calcium tube. The same roll of silver may be used over and over again in many analyses. Only after repeated use will it be necessary to ignite it in a stream of hydrogen. In the analysis of iodine compounds the column of copper turnings may be dispensed with altogether and the silver foil employed by itself.

Kekulé places several pieces of fused chromate of lead in the front part of the combustion tube, to stop chlorine and bromine; and to the same end Vœlcker (*Chemical Gazette*, 1849, 7. 245) recommends that the oxide of copper be mixed with one-fifth its weight of oxide of lead. Compare Method 4.

Substances which contain Fixed Inorganic Constituents may usually be analyzed more readily by the process now in question than by Method 1 (see p. 64), for the ash which remains in the boat after the completion of the combustion can in most cases be weighed. In the analysis of compounds containing K, Na, Ca, Sr, or Ba the amount of carbonic acid retained by the ashes in the boat can sometimes be ascertained by simple calculation and added to the quantity found in the potash bulbs. In case the composition of the ashes cannot be inferred *a priori*, the amount of carbonic acid contained in them had better be determined by fusing the residue with borax glass (see under Carbonic Acid).

Method 3. Combustion with Oxide of Copper, in conjunction with Oxygen gas obtained by heating Chlorate or Perchlorate of Potassium, at or within the combustion tube.

The operation of filling the combustion tube is similar to that described under Method 1, with the exception that the column of oxide of copper at the posterior end of the tube is made about 5 c. m. long, instead of 3 or 4, and is mixed, by shaking, with 3 or 4 grms. of fused chlorate of potassium, in the form of coarse powder. The fused chlorate should be still warm when thrown into the tube. A layer of oxide of copper about 2 c. m. thick should be placed above the chlorate mixture to separate it from that which contains the substance to be analyzed. — After the anterior column of oxide of copper and the mixture of oxide of copper and substance to be analyzed have been heated, as in Method 1, the mixture of chlorate of potassium and oxide of copper is slowly heated, so that the combustion tube may be filled with oxygen gas. Any particles of carbon which the oxide of copper has failed to consume, will now be completely oxidized, as well as the metallic copper which has been reduced in the previous steps of the analysis. The mixture of chlorate of potassium and oxide of copper must be heated with extreme care in order that no great quantity of the chlorate

may be decomposed at once. A tumultuous current of oxygen would be liable to throw some of the potash lye out of the bulbs, and ruin the analysis. After all the reduced copper has been oxidized, the oxygen set free from the chlorate will of course sweep forward the carbonic acid which was contained in the tube, and will fill the potash bulbs and chloride of calcium and soda-lime tubes. To remove this oxygen, connect the bulbs and tubes with an aspirator, after disconnecting them from the combustion tube, and draw through them a quantity of air free from moisture and carbonic acid, before placing them in the room of constant temperature to be weighed.

Instead of placing chlorate of potassium in the combustion tube, Laurent (*Annales de Chim. et Phys.*, (3.) 19. 360; *Gerhardt's Traité de Chim. Organ.*, Paris, 1853, 1. 35) proceeds as follows:—After having dried the combustion tube and thrown a small quantity of warm, coarse oxide of copper into its posterior end, introduce the substance to be analyzed, mix it roughly with a small quantity of warm oxide of copper, and fill the tube with oxide of copper, taken directly from the crucible in which it has been ignited, and still as hot as 200° or 250°. Place the tube in the combustion furnace, and by means of a bent glass tube and rubber connector attach the closed upturned point of the tube with a U-tube, one arm of which is filled with chloride of calcium, and the other with fragments of caustic potash. That arm of the U-tube which is farthest from the combustion tube contains the potash, and is provided with a cork pierced with two holes. One of the holes carries a tube bent at an angle somewhat less than a right angle, and the other carries a straight, upright tube, drawn to a fine point and closed at its upper extremity. The outer end of the bent tube is attached, by means of a perforated cork, to the mouth of an ignition tube of hard glass, 30 or 40 c. m. long, and charged with 3 or 4 grammes of fused chlorate of potassium. The ignition tube rests upon a wire grate in such manner that the chlorate can be heated by placing bits of hot charcoal around the tube. Detach the rubber connector from the posterior point of the combustion tube, and proceed to heat the latter in the usual way. — After the combustion in the tube has been pushed to such an extent that little or no more carbonic acid goes forward, suck a small quantity of air from the open end of the soda-lime tube, in order to establish a partial vacuum within the combustion tube, and crush the end of the upturned point of the combustion tube with a pair of pincers. Slip on the rubber tube which connects the apparatus with the U-tube and the tube charged with chlorate of potassium, and place live coals about the latter so that oxygen may be slowly evolved from it. The tube must be heated very slowly, and care must be taken that the upper part of the tube is kept hot

enough to prevent the solidification there of the melted chlorate. When the oxygen ceases to be absorbed by the reduced copper, and begins to pass rapidly through the potash bulbs, break off the point of the upright tube attached to the U-tube, and draw air through the latter and the rest of the apparatus until the whole of the oxygen has been expelled.

Since chlorate of potassium decomposes with a certain degree of violence, Bunsen recommends that it be replaced by perchlorate of potassium prepared, in the ordinary way, by heating the chlorate. A few grammes of the fused and still hot perchlorate are thrown into the posterior end of the combustion tube, a loose plug of recently ignited asbestos is pushed down to keep the potassium salt in place, and the rest of the tube then filled in the ordinary way. In case the substance to be analyzed is mixed with oxide of copper by means of a twisted wire, as explained on p. 61, perchlorate of potassium should always be used instead of the chlorate.

Non-volatile Liquid Substances. Weigh the substance (a fatty oil for example) in a small glass tube, kept upright by a wire support. Place a quantity of oxide of copper and chlorate of potassium in the end of the rather long combustion tube, as above described, drop in the loaded weighing tube and cause the oil to run out into the combustion tube and spread about upon the surface of the glass, excepting the anterior third or fourth of the tube and the upper side of the tube where the open channel is to be left. Fill the tube with oxide of copper which has been cooled in a tight flask, as described on p. 61, and take care that the weighing tube is filled with the oxide. Place the tube in hot sand, so that the oil may become more fluid and so be completely absorbed by the oxide of copper, and proceed with the analysis as above described. — Solid fats or waxes may be fused in a small weighed boat of glass, made from a tube divided lengthwise, and then cooled and weighed. The boat and contents may then be dropped into a combustion tube, into the end of which oxide of copper and chlorate of potassium have been previously thrown, and heat applied so that the substance may be spread about the tube and subsequently absorbed by the oxide of copper as just described.

Method 4. Combustion with Oxide of copper in conjunction with Atmospheric Air. (Method of Clöëz).

This method of analyzing organic compounds is characterized by the simplicity and cheapness of the apparatus required, as well as by its very general applicability. It may be employed not only for the analysis of compounds of carbon, hydrogen and oxygen, whether solid or liquid, volatile or non-volatile, but for the determination of carbon and hydrogen in substances contaminated with nitrogen, sulphur,

chlorine, bromine, iodine, or fixed inorganic materials.

In some respects the process resembles Method 2, but differs from it inasmuch as a wrought iron pipe is employed as the combustion tube, in place of the glass tube above described, and that atmospheric air is used as an oxidizing agent instead of oxygen gas. Since the iron tube is well nigh indestructible, the apparatus, once mounted, becomes a permanent fixture, and may be used for an almost indefinite number of analyses.

Select a piece of wrought iron gas pipe, about 115 c. m. long and 20 or 22 m. m. in diameter. Provide a combustion furnace about 75 c. m. long, so that each end of the tube shall project 20 c. m. beyond the fire. Heat the tube to redness and pass in a current of steam to oxidize the inner surface of the tube. Fill the middle part of the tube with a long column of coarse, hard oxide of copper, and to keep the oxide of copper in place, plug it with spiral rolls of superficially oxidized copper foil. Provide two boats of stout sheet iron, one 20 the other 30 c. m. long, of such size that they can be readily pushed into or drawn out from the combustion tube; for this purpose attach a short iron wire to one end of each of the boats. The longer boat belongs at the posterior end of the combustion tube, the shorter at the front. If the substance to be burned contains nothing but carbon, hydrogen and oxygen, the anterior boat is to be filled with coarse oxide of copper,—or the boat may be left out altogether in case the substance to be analyzed is readily combustible. If, on the contrary, the substance to be analyzed is nitrogenous, fill the anterior boat with copper turnings (compare p. 64); if it contain sulphur, chlorine, iodine, or bromine, fill the boat either with red lead or with chromate of lead.

Solids. In case the substance to be burned is a solid consisting only of carbon, hydrogen and oxygen, both the boats are filled with oxide of copper and placed in the combustion tube, which is then heated as far as the furnace reaches during 10 or 15 minutes, while a slow stream of air is forced through the tube. Allow the posterior portion of the tube to cool somewhat, then take hold of the tube with a pair of roughened pincers (gas-fitters' pliers), remove the stopper, draw out the boat and cork it up in a special iron tube, kept for the purpose, until it has become well nigh cold. Meanwhile attach the weighed chloride of calcium tubes, etc., to the anterior end of the tube, which has hitherto remained open.

As soon as the oxide of copper is cold enough, place the boat on a sheet of thin copper foil, and with a polished iron hook transfer a portion of the oxide to a small, shallow rectangular box or shovel of brass, open at one end. Quickly scatter the substance to be analyzed over the oxide of copper left in the

boat, cover it with the oxide in the shovel, push back the boat into the combustion tube, replace the stopper and pass a slow current of air through the apparatus. The combustion is conducted in the usual way in so far that the anterior end of the boat is first heated, while the oxide of copper in the middle and front part of the tube is kept red hot. By noting the rate at which the air bubbles pass through the potash lye in the permanent set of purifying tubes behind the furnace, and the weighed potash bulbs in front, it is easy to follow the process of the combustion, and determine when the operation is finished. — Instead of transferring the boat full of oxide of copper to a special cooling tube, it may be left to cool in the combustion tube if the operator prefer.

After the combustion is finished, and the weighed absorption tubes have been removed to the room of constant temperature, force a strong current of air through the tube in order to reoxidize the reduced copper, and proceed to the next analysis.

Liquids. Non-volatile liquids are weighed in a tube drawn out to a fine point, and are then transferred to the oxide of copper in the boat; the weight of the substance taken is determined by weighing the empty tube. Volatile liquids may be weighed in a tube provided with a glass stopper at one end, and drawn out to a point at the other. This tube is laid on the oxide of copper in the boat, the stopper is removed, the boat immediately pushed into the combustion tube, and a slow stream of air forced through the tube. In this case the oxide of copper in the posterior boat is not heated until the stream of cold air has ceased to carry forward vapors of the substance into the column of hot oxide at the middle of the tube.

Nitrogenous Substances. In analyzing nitrogenous substances, a copper boat filled with copper turnings (see Nitrogenous substances under Methods 1 and 2) is placed in the fore part of the tube, and only a very slow stream of air is kept up during the first part of the combustion. The current of air may be made more rapid towards the close of the analysis, though the anterior portion of the layer of metallic copper should remain unoxidized to the last.

Sulphur, Chlorine, Bromine or Iodine. In the analysis of substances containing sulphur, chlorine, bromine or iodine, the anterior boat is filled with dry red lead or chromate of lead, and the substance is mixed with fused and powdered chromate of lead in the posterior boat. The anterior boat should be heated only to incipient redness, in order that its contents may not fuse.

Ash Determinations. In case the proportion of ashes in the substance analyzed is to be determined as well as the carbon and hydrogen, weigh the substance in a porcelain boat, place

the latter on a piece of platinum foil turned up at the edges and provided with a wire for withdrawing it from the tube, push the boat up to the permanent column of oxide of copper in the middle of the tube, and proceed with the combustion in the ordinary way. After the products of the dry distillation of the substance have been consumed, the residual carbon is burnt at the expense of the oxygen in the stream of air. A somewhat longer time is required in this case than when the combustion is finished in oxygen, but the results obtained are said to be equally accurate.

To dry and purify the air required for this process, Cloëz employs a set of permanent tubes and flasks, consisting: 1st, of a small bottle containing dilute potash lye,—the tube which brings air to this flask barely dips beneath the surface of the liquid; 2d, of a tall, drying cylinder, filled with bits of pumice stone soaked in sulphuric acid; 3d, of a long horizontal tube, with turned-up ends, filled with porous chloride of calcium; and 4th, of a similar tube filled with fragments of caustic potash.

Instead of a weighed chloride of calcium tube to absorb the water produced by the combustion, he employs a U-tube filled with fragments of pumice stone moistened with oil of vitriol. (Cloëz, *Annales Chimie et Phys.*, (3.) 68. 394.)

Method 5. Combustion in Atmospheric Air, in conjunction with Oxide of Copper. (Method of Fresenius).

This method is applied to the estimation of the chemically combined carbon in cast or wrought irons, particularly in those kinds of iron which contain much graphite and but little combined carbon.

Method. Reduce a quantity of the iron to fine powder. Weigh out from 1 to 1.5 grms. of the powder, and place it in a flask of about 150 c. c. capacity. Fit a two-holed caoutchouc stopper to the flask, and to one of the holes fit a glass tube rather more than twice as long as the flask is high. Bend this tube twice near the middle into the form of an S, in such manner that the bent portion may be wholly outside the cork, while enough of the tube is left straight at either end to reach almost to the bottom of the flask; blow a small bulb at the middle of the bent portion, i. e., at the centre of the S. After the S-tube has been fitted to the stopper, pour a few drops of quicksilver into the lower bend of the S. To the other hole in the stopper fit a delivery tube. This delivery tube should pass straight upwards through a distance about as great as the height of the flask, and then bend at a right angle to meet a horizontal combustion tube. Before fixing this delivery tube to the stopper, slip a short piece of rather wide glass tube over its upright part, and by means of a perforated cork fasten the lower end of this

outer sleeve tightly to the delivery tube. During the experiment, this sleeve is kept full of water to cool the mixture of air and hydrogen passing forward from the flask.

The combustion tube may be about 30 c. m. long. Half its length—the end next the flask,—is filled with loosely packed asbestos and the other half with coarse oxide of copper, the latter being kept in place by a final plug of asbestos. To the end of the combustion tube which is farthest from the flask attach a large unweighed U chloride of calcium tube, to the latter attach a small, weighed soda-lime tube, and beyond the soda-lime place another unweighed U-tube, filled half with soda-lime and half with chloride of calcium, to protect the weighed tube. To this last U-tube attach an aspirator.

Ignite the contents of the combustion tube in a current of air free from carbonic acid; connect the combustion tube with the delivery tube of the flask, test the tightness of the apparatus, and heat the oxide of copper half of the combustion tube to low redness. Place a small thistle tube in the top of the S-tube of the flask, fill the thistle tube with dilute sulphuric acid, made by mixing 1 part of strong acid with 5 parts of water, and by means of the aspirator draw over into the flask, past the mercury, a quantity of the acid sufficient to dissolve the iron. Remove the thistle tube, replace it with an unweighed soda-lime tube, attach the latter to the S-tube with a caoutchouc connector and, by means of the aspirator, draw a slow current of air through the apparatus while the iron is dissolving. — Heat the flask carefully in a water bath, or upon a metallic plate, so that the iron may dissolve with tolerable rapidity.

The mixture of air, hydrogen and carburated hydrogen burns to water and carbonic acid, at the edge of the asbestos in the combustion tube, so completely that but little of the oxide of copper in the combustion tube is ever reduced. In case any of the oxide of copper happens to be reduced for a moment the metal is immediately reoxidized by the excess of air. The column of asbestos prevents the possibility of the flame's passing back into the flask. The carbonic acid formed during the combustion is absorbed in the weighed soda-lime and its amount determined by reweighing the tube at the close of the experiment.

As soon as the evolution of hydrogen ceases, heat the column of asbestos in the combustion tube in order to oxidize any traces of hydrocarbons which may have condensed on the asbestos, and afterwards allow the apparatus to cool in a slow current of air. Weigh the soda-lime tube and from the weight of carbonic acid thus found calculate that of the carbon which has been evolved from the iron as a gaseous compound. The traces of hydrocarbons retained by the iron solution in the flask are

practically insignificant, though sufficient to impart an odor to the liquid.

The iron in the flask of course dissolves more or less rapidly, according to the kind of metal, the fineness of the powder and the degree of heat, but as a rule the experiment requires 1 or 2 hours for its completion. — In operating upon samples of iron containing but little graphite it may be well to throw into the flask a small quantity of platinum sponge to accelerate the solution. — The process is inapplicable for the analysis of certain kinds of iron which deposit a portion of the combined carbon in the solid form (together with the graphite) when treated with dilute sulphuric acid. (Buchner, *Journ. prakt. Chem.*, 72. 364). It is easy to determine whether carbon has been thus deposited in any given case by examining the residual graphite. To this end notice, in determining the Graphite, whether any coloration is imparted to the liquids, — boiling water, potash lye, alcohol, and ether, — with which the graphite is washed. Observe also whether the alcohol or ether, with which the graphite has been washed, after removal of the potash lye by water, leave any residue of organic matter when evaporated. (Fresenius, *Zeisch. analyt. Chem.*, 1865, 4. 73). The process yields accurate results. (Compare Tosh, *Chem. News*, 1867, 16. 67).

Method 6. Combustion with Oxygen gas. (Warren's method).

Specially adapted for the analysis of volatile liquids, and of gases.

Bend a combustion tube in the manner described under Method 2, in the paragraph relating to volatile liquids; pack the horizontal part of the tube with small, fibrous pieces of asbestos, or other inert substance, so loosely that gases may pass freely through all parts of the mass, and at the same time so closely that no mixture of oxygen and hydrogen or other inflammable gas can explode when heated in its midst. In packing the tube, the asbestos should be added little by little and each new portion pressed gently against the preceding by means of a stiff wire. Little attention need be paid to the arrangement of the asbestos in the middle of the tube, since that portion of the column will come right of itself if the material is properly packed against the glass. A good way is to hold the tube in the left hand and turn it continually, while the wire in the other hand is made to pass around against the sides of the tube, gently tapping the asbestos and compressing it so that only very small open spaces can be seen in the finished column. It is best to make the horizontal part of the tube long enough to hold a column of asbestos 10 or 12 inches long, and to place a short column (2 or 3 inches) of coarse oxide of copper in front of the asbestos as a safeguard against accidents.

The substance to be analyzed is introduced

at the posterior part of the tube in the manner described in the paragraph just cited, and the analysis is conducted as there directed. Special care must, however, be exercised in regulating the stream of oxygen so that an excess of this gas may always be present in the combustion tube. To this end, the permanent drying apparatus should contain a set of potash bulbs of the same size as the weighed potash bulbs at the front of the tube, so that the number of bubbles, that is to say volumes, of oxygen entering the tube may be readily compared with the bubbles of carbonic acid which pass out. About 2 vols. of oxygen should be made to pass through the posterior potash bulbs for every bubble of mixed carbonic acid and oxygen which appears at the anterior bulbs. Or, better, the posterior set of bulbs may be made of such size that each of their bubbles shall be twice as large as those of the anterior bulbs. In case the supply of oxygen were at any time decidedly deficient the fact would be indicated by the reduction of some of the oxide of copper at the front of the tube. For a description and figure of an attachment for saving the excess of oxygen, and at the same time preventing the possibility of losing an analysis through the escape of unconsumed carbonaceous gases see Warren's original memoir, as cited below.

In spite of the fact that by far the larger part of the substance is consumed in a very small portion of the column of asbestos, it has not been found advisable to make the combustion tube any shorter than has been recommended above. With a short tube it is far more difficult to control the distillation of the substance and to regulate the supply of oxygen. The method of preventing any of the substance from escaping backwards from the combustion tube has been already described. See Method 2, paragraph on Volatile liquids. (Warren, *Amer. Journ. Sci.*, 1864, 38, 387).

Method 7. Combustion with Oxygen after volatilization in a stream of Hydrogen. (A. Mitscherlich's method).

Applications. Simultaneous estimation of C, Cl, Br, I, S, and N in solid, liquid, or gaseous, substances without need of any combustion furnace.

Method. Heat the substance to be analyzed in a stream of hydrogen, and burn the hydrogen, thus charged with the vapor or products of distillation of the substance, in a stream of oxygen. If the substance contains no sulphur, pass the products of the combustion over a sheet of strong sulphuric acid to remove the water, then through a strong solution of nitrate of lead to absorb the chlorhydric acid, next through a tube filled with oxide of mercury to absorb bromine, and then through potash lye to absorb the carbonic acid. Finally pass the residual nitrogen and the excess of oxygen through a tube containing phosphorus, in order

that the oxygen may be absorbed, and collect and measure the nitrogen in a graduated cylinder.

The amounts of Cl, Br and C are determined by weighing the several absorption tubes before and after the experiment.

If the substance contains sulphur, replace the solution of nitrate of lead with a concentrated solution of bichromate of potassium to absorb the sulphurous acid. In order to get rid of a small quantity of sulphuric acid which is formed during the combustion of the mixed hydrogen and sulphur compound, place some chloride of calcium and a little sulphite of calcium near the hydrogen flame. The moist sulphuric acid is absorbed by the sulphite of calcium as fast as it is formed, and at the same time a quantity of sulphurous acid, equivalent to that of the sulphuric acid, is set free from the sulphite to be absorbed by the chromate of potassium in due course. — If the substance contains iodine, the latter is allowed to deposit itself near the hydrogen flame at first and is subsequently sublimed into a clean glass tube, of known weight, and weighed as such.

In case any portion of the substance remains unvolatilized after having been thoroughly heated in the stream of hydrogen, the residue is weighed directly and estimated either as carbon or ash, as the case may be. For the details of this interesting process, see A. Mitscherlich's memoir in *Zeitsch. analyt. Chem.*, 1867. 6. pp. 151–166, and 141.

Method 8. Combustion with Chromate of Lead.

This method was formerly much employed as a substitute for Method 1, in analyzing difficultly combustible substances, such as resins, coal, fats, etc.; it is, however, less convenient than Methods 2, 4 and 6.

Anderson (*Annalen Chem. und Pharm.*, 122. 300) has observed but cannot explain the fact that in analyzing hydrocarbons with pure chromate of lead, the amount of hydrogen found is often considerably larger than it should be.

The details of the process, which may be used for analyzing solids and liquids, whether volatile or non-volatile, are similar to those of Method 1, with the exception that fused, powdered chromate of lead is substituted for the oxide of copper. The combustion tube need not be so large as in Method 1, since chromate of lead contains far more available oxygen than an equal volume of oxide of copper. (See Chromate of Lead). The chromate is simply heated in a porcelain or platinum dish, over a lamp, until it begins to turn brown, and then allowed to cool at 100°, or to a lower temperature, before it is transferred to the combustion tube or mixing mortar. Since chromate of lead is as hygroscopic as oxide of copper, the tube must finally be dried with an exhausting syringe, as described under Method 1.

The combustion is conducted in the same

way as with oxide of copper, but towards the close that part of the tube which contains the substance must be heated intensely, in order to fuse the chromate of lead so that no particles of carbon may escape combustion. This power of fusing at a moderate heat is one of the chief advantages of the chromate as compared with oxide of copper. Care must be taken, however, not to fuse the chromate at the anterior part of the tube, nor to heat it so hot that it shall lose its porosity, lest it become powerless to act upon gaseous products which have been only incompletely oxidized at the other end of the tube. It is well, for that matter, to fill the anterior part of the tube with coarse oxide of copper instead of chromate of lead, or with copper turnings which have been superficially oxidized by heating them in the air.

For the use of bichromate of potassium in conjunction with chromate of lead, see below, Method 9.

Sulphur Compounds may be burned with chromate of lead in a tube 60 or 80 c. m. long, if care be taken that 10 or 20 c. m. of the fore part of the column are never heated above low redness. (Carius, *Annalen Chem. und Pharm.*, 116, 28). For the use of chromate of lead in conjunction with oxide of copper and air, see above, Method 4.

Chlorine and Iodine Compounds may be analyzed with chromate of lead without the risk of errors such as are liable to occur when oxide of copper is used. The chlorine or iodine is converted into chloride or iodide of lead and so retained in the combustion tube.

Some Bromine Compounds, however, are not readily analyzed in this way, since the metallic bromide formed during the combustion is liable to fuse and enclose some particles of carbon so completely that they cannot be burned. To avoid this difficulty Gorup-Besanez, *Zeitsch. analyt. Chem.*, 1862, 1. 439 recommends the following method:—Choose a combustion tube with a rather long, upturned point, place in the tube a three-inch layer of oxide of copper, then a plug of asbestos, then a porcelain boat containing the substance to be analyzed in fine powder, mixed with about an equal weight of dry oxide of lead; then another asbestos plug, a column of granular oxide of copper, and finally chromate of lead or copper turnings. First heat to redness the anterior and posterior portions of the tube, and then warm the tube at the boat very carefully and gradually. The combustible portions of the substance will distil over in the form of vapor and be burnt by the hot oxide of copper, and nothing but bromide and oxide of lead will be left in the boat. Complete the combustion in a stream of oxygen, taking care that no more of the gas is passed than is necessary and that the contents of the boat are not too strongly heated. To prevent bromide of copper from subliming into the chloride of calcium tube, see Method 2, p. 68.

Method 9. Use of Bichromate of Potassium.

A. Bichromate of Potassium with Chromate of Lead. In analyzing some very difficultly combustible substances, such as graphite, for example, it has been found advantageous to mix the chromate of lead with about one-tenth its weight of fused and powdered bichromate of potassium. This mixture melts readily and gives off towards the close of the process a little more oxygen than would be evolved from mere chromate of lead. (Liebig; Mayer, *Annal. Chem. und Pharm.*, 95, 204). The mixture of chromate of lead and bichromate of potassium is well fitted also for the analysis of organic compounds containing potassium, sodium, barium, calcium or strontium. No trace of carbonic acid is retained by either of these metals when their compounds are ignited in presence of the mixed chromates.

B. Bichromate of Potassium with Oxide of Copper. It has been suggested by Rochleder that a fused mixture of oxide of copper and bichromate of potassium might be used instead of chromate of lead for burning difficultly combustible substances, and, considered merely as an oxidizing agent, the mixture is said to yield excellent results. But the fused mass is so hard to pulverize that it is practically less convenient than chromate of lead.

Schulze has employed these ingredients in a somewhat different way for determining the proportion of humus in soils. His process is as follows:—Rub 10 grms. of the finely powdered and sifted soil together with 20 grms. of a mixture of equal parts of oxide of copper and bichromate of potassium. Place the mixture in the closed end of a combustion tube, put a layer of oxide of copper in front of the mixture, a layer of finely divided metallic copper in front of the oxide of copper, and leave a space of several inches empty at the front of the tube. Connect the anterior end of the tube with the collecting bottle of Schulze's apparatus for estimating carbonic acid (see Carbonic Acid, estimation of by measuring the gas), turn down the water delivery tube of the connecting bottle and proceed to heat the mixture in the combustion tube precisely as in an ordinary combustion; *i. e.*, from the front backwards, taking care not to heat the tube so strongly as to distort it. Measure the water expelled from the collecting jar, as directed in the paragraph above referred to, in order to determine the volume of carbonic acid. — The metallic copper at the front of the tube will retain any oxygen which may be given off from the bichromate. A special experiment must be made, as directed under Carbonic Acid, in order to ascertain how much of the carbonic acid obtained by the combustion is derived from carbonate of calcium in the soil. The difference between the two determinations will give the amount of carbonic acid derived from the carbon burnt. In case the carbonic acid is mixed with nitrogen or

other foreign gas, it may be passed into baryta water and precipitated as Carbonate of Barium. (Schulze, *Zeitsch. analyt. Chem.*, 1863, 2. 298).

Another method of employing the two ingredients, is to mix them in the combustion tube, as has been proposed by Gintl (*Zeitsch. analyt. Chem.*, 1863, 7. 302). — Into an ordinary combustion tube, drawn up to a point and closed at one end, pour a layer of about two inches of coarse oxide of copper, then a layer of several inches of fused and powdered bichromate of potassium, then the organic substance to be analyzed and then a layer of several inches of oxide of copper. Both the powdered bichromate and the oxide of copper are kept free from moisture in tightly closed tubes or flasks, as explained on p. 61. By means of a twisted wire (Compare p. 61), mix the substance, the oxide and the bichromate intimately, then fill the anterior part of the tube with oxide of copper and proceed with the combustion in the usual way. (See Method 1). Since some free oxygen resulting from the partial decomposition of the bichromate is apt to escape from the tube, care must be taken at the close of the combustion to draw air through the apparatus until the last trace of oxygen gas has been displaced from the potash bulbs.

The process yields excellent results, the combustion is easily completed at a comparatively low temperature and the materials employed are much cheaper than chromate of lead.

C. *Bichromate of Potassium with dilute Sulphuric Acid.* (Method of analysis by gentle or "Limited" oxidation). Compare Brunner (below, under Method 10).

Many organic substances, such, for example, as the fatty acids, undergo no change when treated with a dilute solution of bichromate of potassium mixed with weak sulphuric acid; while other substances, such as compounds of lactic acid and diethoxalic acid are readily decomposed by the mixture, with evolution of a definite quantity of carbonic acid. Hence it is possible to analyze certain mixtures of organic compounds, — after the mode of decomposition of the easily oxidizable constituents has once been determined, — by heating the mixture with the acidulated solution of bichromate and collecting and weighing the carbonic acid which is formed.

For decomposing one class of substances, such as the lactates, Chapman & M. Smith (*Journal London Chem. Soc.*, 1867, 20. 173) employ the following process:—Place a weighed quantity of the substance to be analyzed in a wide-mouthed flask, and fit to the flask a caoutchouc stopper with two perforations. In one hole of the stopper place a short delivery tube bent at a right angle, and in the other hole a long tube reaching almost to the bottom of the flask, provided with a bulb above the stopper, and closed at the upper end with a bit of caoutchouc tubing and glass plug. To the delivery

tube attach a Will & Varrentrap's nitrogen bulb filled with concentrated sulphuric acid and set in a basin of cold water; to the nitrogen bulb attach a set of Liebig's potash bulbs, and to the latter attach a small tube filled with fragments of solid hydrate of potassium. Since the purpose of the sulphuric acid is merely to purify the carbonic acid, it need not be weighed, but both the potash bulbs and tube must be weighed before and after each experiment. — Prepare a quantity of the oxidizing solution by placing 100 grammes of bichromate of potassium and 125 grms. of oil of vitriol in a litre flask and filling the flask with water to the mark. Pour about 150 c. c. of this solution through the bulb-tube into the flask, close the tube with the plug, and heat the contents of the flask upon a water bath. The carbonic acid set free is dried and otherwise purified by the sulphuric acid in the nitrogen bulbs, and is absorbed by the potash in the weighed apparatus beyond. In the course of 20 minutes bubbles of carbonic acid cease to pass through the sulphuric acid, and a quantity of the potash lye rises into the large bulb of the Liebig apparatus. When this occurs, remove the plug from the top of the bulb-tube at the flask, attach a soda-lime tube to the bulb-tube to purify the air, and by means of an aspirator draw air through the flask until all the carbonic acid has been swept forward. The increase in weight of the potash bulbs and tube gives the amount of carbonic acid which has been evolved from the substance. — It is important to keep the sulphuric acid in the nitrogen bulbs cool, lest it act upon some of the aldehyde or other volatile products of the decomposition, which pass forward with the carbonic acid, and so generate sulphurous acid. Since the province of the sulphuric acid is to absorb aldehyde as well as water, chloride of calcium cannot be used in its place.

Another form of apparatus employed by Chapman & Smith in certain cases for estimating the carbonic acid by loss, is figured on p. 180 of their memoir.

Method 10. Combustion with Chromic Acid.

This process is used for estimating carbon in east-iron (see above, Principle 1, D), and for determining carbon in soils, vegetables and other substances whose ashes would be likely to interfere with the ordinary methods of analysis. Like Method 7 it differs essentially from Methods 1 to 6 and 8, inasmuch as it is applicable to the determination of carbon without regard to the hydrogen which usually accompanies this element.

Provide a two-necked flask of about 150 c. c. capacity. To one neck of the flask fit a perforated cork carrying a tube bent at a right angle, and to the other opening attach a wide tube provided with a bulb of 70 or 80 c. c. capacity. The purpose of this bulb is to condense aqueous vapor generated in the flask; it

must be supported in a vertical position above the flask. The inner limb of the right-angled tube above mentioned must be long enough to reach to the bottom of the flask; the other limb extends a few inches outwards from the cork and is plugged at the end with a bit of glass rod fitted to a short piece of rubber tubing. Set the flask in a basket of wire gauze on a ring of a lamp-stand. Connect the vertical bulb-tube with a permanent drying apparatus consisting of a cylinder of about one-quarter litre capacity, filled with pumice stone, which has been soaked in strong sulphuric acid and afterwards heated to expel any traces of chlorhydric or fluorhydric acid which may have been contained in the stone, and a U-tube about 60 c. m. long full of chloride of calcium. To absorb the carbonic acid, attach to the chloride of calcium tube a small, weighed U-tube, full of soda-lime or potash-pumice, with a short layer of chloride of calcium at the outer end.

In case the substance to be analyzed consists of the residue from 2 grms. of cast iron, as explained on p. 58, the details of the process will be as follows:—Remove from the flask the cork which carries the right-angled tube, and draw up the inner limb of this tube through the cork so that it shall not reach far into the flask. By means of a wash bottle with fine jet, wash the carbonaceous matter into the flask, taking care to use as little water as possible. If the quantity of liquid in the flask does not exceed 25 c. c. add to it 40 c. c. of concentrated sulphuric acid, or a proportionally larger quantity of acid if the volume of water is larger, and allow the mixture to cool. Attach the flask to the system of drying and absorption tubes, throw into it about 8 grammes of solid chromic acid, free from potassium, and immediately replace the cork. — Heat the flask gradually until the evolution of gas becomes so violent that the mixture threatens to boil over, and maintain the temperature at this point as long as there is a lively evolution of gas. When the current of gas slackens, heat the flask more strongly until white fumes appear in the vertical bulb-tube, and maintain the mixture at this temperature until the evolution of gas becomes very weak. Attach an aspirator to the weighed soda-lime tube and open its cock slightly; push down the right-angled tube in the flask until it dips beneath the surface of the liquid, remove the plug from the outer limb of the right-angled tube, and attach to the latter a tube filled with fragments of caustic potash. Then open the cock of the aspirator somewhat wider, so that bubbles of air may pass through the liquid in the flask at the rate of about 2 a second. When 5 or 6 litres of water have flowed from the aspirator the whole of the carbonic acid will have been swept out of the apparatus and absorbed in the weighed soda-lime tube. Allow the latter to cool before weighing it.

In using this method for determining carbon in an organic substance, about 16.6 grms. of chromic acid and 25 c. c. of concentrated sulphuric acid should be taken for every gramme of the substance. About 2 vols. of water should be placed in the flask for every 3 or 4 vols. of strong sulphuric acid used. If the organic substance contains chlorine, bromine or iodine, a tube filled with pulverulent iron, copper or silver must be placed between the vertical bulb-tube and the permanent drying cylinder to absorb the foreign gas. (Ullgren, *Annal. Chem. und Pharm.*, 124. 59). — Ullgren prefers chromic acid to the bichromate of potassium recommended by the brothers Rogers, and by Brunner (*Pogg. Ann.*, 95. 379), since it is possible in this way to avoid the formation of an annoying precipitate of anhydrous chrome alum which interferes with the reaction, when bichromate of potassium is employed. The chrome alum thus thrown down as a green, slimy powder, almost insoluble in water, acids, or alkalies, not only delays the oxidation, but tends to conceal its completion. — According to Brunner, it is possible, by his process, to estimate the ordinary modification of carbon in presence of graphite, by oxidizing first with a mixture of bichromate of potassium and dilute sulphuric acid and afterwards using strong acid; but the separation did not succeed in Ullgren's hands. For the application of this process to organic analysis, compare W. Knop, *Chem. Centralblatt*, 1861, p. 17.

Method 11. Combustion with a mixture of Chromate of Lead and Chlorate of Potassium.

Applications. Estimation of carbon in cast-iron.

Method. Close a combustion tube of hard glass at one end and place at the closed end a two-inch layer of a mixture of equal parts of chromate of lead and chlorate of potassium. Mix about 3 grms. of the finely powdered iron with 50 grms. of a mixture of 40 parts chromate of lead and 6 parts of fused chlorate of potassium, and place the mixture in the combustion tube. Finally, place a layer of chromate of lead in front of the mixture, and connect the tube with a chloride of calcium tube and a weighed soda-lime tube or set of potash bulbs. Heat the contents of the combustion tube carefully, beginning at the anterior end. When the mixture of iron and the oxidizing agents is heated to dull redness the metal burns with incandescence, and the carbon contained in it is converted into carbonic acid. At the close of the operation the free oxygen evolved from the mixture of chlorate and chromate at the end of the tube sweeps forward the carbonic acid and, if need be, completes the oxidation of the iron. — The process usually yields good results, though the percentage of carbon found is sometimes rather lower than the truth. The addition of chlorate of potassium is essential to

success in determining carbon in cast-iron; with chromate of lead alone the amount of carbon obtained from the cast-iron is always too small. (Regnault, *Annal. Chem. und Pharm.*, 30. 352; Bromeis, *Ibid.*, 43. 241; Tosh, *Chem. News*, 1867, 16. 67). Take care to remove the oxygen from the absorption tube before weighing. Or, instead of that, the soda-lime tube may be filled with oxygen in the first place, and always be weighed full of oxygen.

Method 12. Combustion with Chlorate of Potassium.

The original process of Gay-Lussac & Thénard was as follows:—An intimate mixture of known weights of chlorate of potassium and of the substance to be analyzed was made into small pellets and the latter were thrown, one by one, with proper precautions, into a vertical tube kept at a red heat. The carbonic acid, oxygen and nitrogen (if present) were conducted through a lateral delivery tube to a mercury trough and there collected in a graduated cylinder. After the total volume of gas had been measured, the amount of carbonic acid was determined by absorption with caustic potash and that of the oxygen by exploding the residue with hydrogen in a eudiometer.

The process was faulty, as regards nitrogen compounds, since a portion of the nitrogen was converted into nitrous acid. It was inapplicable, moreover, to the analysis of liquids or of volatile substances. Berzelius improved it by heating the mixture of chlorate and substance in a horizontal tube and collecting and weighing the water generated by the combustion. There was consequently no longer any need of weighing the chlorate of potassium. He mixed the chlorate, moreover, with a large proportion of chloride of sodium, in order that the combustion might be tranquil.

The use of chlorate of potassium in this way was, however, soon given up, and the process superseded by that in which oxide of copper is employed. Quite recently, suggestions have again been made in favor of employing the chlorate in certain cases. Mène (*Comptes Rendus*, 56. 446) recommends the following method. Close one end of a glass combustion tube about 1 m. m. thick, 50 c. m. long and 1 c. m. in diameter, throw in enough fused and powdered chlorate of potassium to fill 2 c. m. of the length of the tube, fill the rest of the tube almost completely with an intimate mixture of the substance to be analyzed and of fused and powdered chlorate of potassium, and secure the whole by placing a plug of asbestos at the front of the column. In making the mixture proceed as follows:—Measure out in the tube itself as much of the chlorate of potassium as the tube will hold, pour out all but the last 2 c. m. of the chlorate, mix it with the weighed and finely powdered substance and pour back the mixture into the tube through a funnel. Since, according to Mène, the fused

chlorate is scarcely at all hygroscopic, the mixing and transfer of the substance may be made at the ordinary temperature without special precautions.

Hang the combustion tube, or support it upon wires, in a horizontal position, attach the weighed absorption apparatus (a large chloride of calcium tube and a couple of soda-lime tubes will be best) and proceed to heat the mixture of chlorate and substance with a single small spirit lamp or Bunsen's burner. The tube is first heated at the asbestos plug and then backwards step by step, until each portion of the chlorate has been melted and made to react upon the organic matter. It often happens that the reaction is attended with evolution of light or even deflagration, particularly when the substance contains a large proportion of carbon, but the deflagration, according to Mène, does no harm even when potash bulbs are used to collect the carbonic acid. At the close of the combustion, the last traces of carbonic acid are swept forward out of the tube by the oxygen set free from the pure chlorate of potassium at the end of the tube. Care must be taken that the absorption apparatus is either weighed full of oxygen at the start, or that air is drawn into it after the combustion. The entire operation lasts only 20 minutes. It is to be observed that the process requires no special furnace and that by means of it a comparatively large weight of the substance may be taken for each analysis.

Another method, proposed by Schulze, is adapted to the analysis of very small quantities of carbon compounds. A mixture of weighed quantities of the substance to be analyzed and of fused, powdered chlorate of potassium is sealed up and ignited in a combustion tube of known capacity, after the air has been pumped out of the tube; and the mixture of gases resulting from the combustion is measured and analyzed by the methods of absorption and eudiometry ordinarily employed in gas analysis. — The combustion tube is made of glass of the quality and strength usually employed for organic analyses, but the capacity of the tube to be selected should be determined approximately by reference to the supposed composition of the substance to be analyzed. In the case of sugar, for example, 16 milligram. of oxygen would be half as much again as is absolutely necessary for the combustion of 10 milligram. of sugar. The gas given off from the quantity of chlorate of potassium, about 41 milligram., necessary to produce 16 milligram. of oxygen would occupy a space of about 12 c. c., measured at the ordinary temperature and pressure. But if this amount of gas were enclosed in a tube of 25 c. c. capacity and heated to 500° or 600°, only a comparatively feeble pressure could be exerted by it upon the walls of the tube. It may be admitted that 100 milligram. of chlorate of potassium

yield 20.805 c. c. of oxygen, and that 1000 c. c. of oxygen at 0° and under the pressure of 1 metre of mercury, weigh 1.8819 gramme.

The combustion tube is drawn out to a point at one end and the point closed; the mixture of substance and chlorate is poured into the tube in such manner that no portion of the mixture shall remain adhering to the tube near the open end. The tube is then drawn out at the lamp near the open end, to a conical point fit to receive a caoutchouc connector. Behind this point the tube is narrowed to such an extent that it can be readily closed at any moment by touching it with a blowpipe flame. Neither the point nor the depression in the tube must be made too thin, lest the glass give way when the tube is exhausted of air.

To exhaust the tube, fit to its aperture a flexible pipe which has been rendered impermeable to air by soaking in hot linseed oil, and connect the other end of the pipe with an air pump, the precise degree of efficiency of which has been determined beforehand by experiments on empty tubes and flasks. Schulze found that the pump employed in his experiments could remove all but 0.001715 of the original volume of air, so that for a combustion tube of 50 c. c. capacity a residuum of 0.08575 c. c. of air had to be allowed for, in calculating the results of an analysis.

When the tube has been exhausted as completely as possible, close it by throwing a blowpipe flame against the narrow place behind the rubber connector, place the tube in an iron gas-pipe a little larger than itself, and heat the iron almost to redness during 20 minutes, over a row of Bunsen's burners. In case several analyses are to be made, a couple of combustion tubes may be placed end to end in the same iron pipe, and heated together. After the lamps have been extinguished, the apparatus may be cooled by pouring water upon the iron. As a general rule the glass tubes may be withdrawn from the gas-pipe half an hour after the lamps were lighted.

To collect the gaseous products of the ignition, provide a rather tall, tubulated bell-glass about 3 c. m. in diameter, to the neck of which has been cemented a fine steel stop-cock connected with a straight projecting tube about 3 m. m. long by 1 m. m. in diameter. Immerse the posterior end of the combustion tube in mercury contained in a tall cylinder, break off the lower point of the tube in the mercury, push the tube down into the mercury and place the bell-glass full of mercury over the top of the tube. Then break the upper, anterior point of the combustion tube so that the contents of the tube may rise into the bell. From the bell the gas may be readily transferred to a measuring tube by simply sinking the bell beneath the tube and opening the stop-cock. — After the total volume of gas has been measured, with the proper precautions, the carbonic acid

is determined by absorption with hydrate of potassium, in the usual way.

Since the fundamental idea of the method is to operate upon very small quantities of material, a very accurate balance is required. According to Schulze, the balance should be delicate enough to indicate, at the least, quantities as small as $\frac{1}{100}$ of the substance weighed. Balances on the principle of that of Ritchie (*Phil. Trans.*, 1830, p. 402; see also *Karsten's allgemein. Encyclop. der Physik*, Lief. 16. p. 606) may be employed with advantage.

Hygroscopic substances may be weighed, and analyzed in the moist condition, it being only necessary to determine the proportion of moisture by drying a special portion of the material. (F. Schulze, *Zeitsch. analyt. Chem.*, 1866, 5. 269.)

Carbonates (various).

Principle. Decomposition of by acids. See Carbonic Acid (Volatility of); and Alkalimetry.

Carbonic Acid. Compare the various Carbonates, below, notably the carbonates of barium, calcium, and mercury. — It may be here remarked that for estimating the amount of carbonic acid in normal carbonates of the alkalies and alkaline earths, it is well to determine the base by means of a standard acid (see Alkalimetry) and to calculate upon the amount of base an equivalent quantity of carbonic acid.

Principle I. Affinity for alkalies.

Applications. Estimation of carbonic acid. Separation of carbonic acid from other gases. Estimation of carbon in organic compounds.

Methods. See Hydrate of Potassium; Soda-Lime, and Carbon. Compare also, below, Carbonic Acid (Volatility of; absorption of the gas in alkali); and Hydrate of Calcium.

Principle II. Volatility.

Applications. Estimation of carbonic and boracic acids. Separation of carbonic acid from all the bases and from all other acids. Alkalimetric determination of the commercial value of the carbonates of sodium and potassium. Estimation of carbonate of calcium and similar carbonates. Acidimetric determination of the value of commercial acids. Indirect separation of strontium from calcium.

Method A. By simple ignition. This method is applicable to the estimation of carbonic acid in all carbonates, — such as those of Mg, Cd, Zn, Pb, Cu, Ni, etc., — which give off the acid readily and completely on being heated. Even with carbonate of calcium carbonic acid can be determined in this way, if only a small quantity of substance be operated upon and the heat be made intense.

If the carbonate to be analyzed is anhydrous, and contain no metal liable to form a mixture of several oxides, when heated, it will be enough to ignite a weighed quantity of it in a crucible until the weight of the crucible and

contents remains constant. The loss of weight will represent the carbonic acid. In case carbonate of lead, carbonate of cadmium, or any other easily reducible carbonate is to be analyzed, the crucible must be of porcelain.

If the residual oxide is prone to absorb oxygen when heated in the air, replace the crucible with a bulb-tube of hard glass, and pass a stream of carbonic acid through the tube during the process of ignition. This method yields very accurate results.

If the substance to be analyzed contains water, it is sometimes possible to estimate the water before the carbonic acid, by first heating a weighed quantity of the material gently until the water has been expelled, and afterwards intensely to drive out the carbonic acid. In case the water cannot be determined in this way it may be estimated as follows:— Weigh out a quantity of the substance in a small boat, and place the latter in a tolerably wide glass tube. By means of dry, tight corks, attach a weighed Chloride of Calcium tube to one end of the wide tube, and an unweighed chloride of calcium tube to the other end. Connect the other end of the weighed chloride of calcium tube with an aspirator, and draw a slow stream of air through the apparatus. Heat the boat and, from time to time, the whole of the wide tube, until all the carbonic acid and water have been expelled from the carbonate and carried forward into the chloride of calcium tube. Allow the apparatus to cool and weigh the boat and the chloride of calcium tube. The difference between the first and second weights of the contents of the boat gives the total amount of carbonic acid and water; the increase in weight of the chloride of calcium tube gives the amount of water, and the difference between the two, the carbonic acid. — Care must be taken neither to leave any moisture in the wide tube nor to burn its corks. To prevent the possibility of any moisture passing back from the aspirator into the weighed chloride of calcium tube, it is well to interpose an unweighed chloride of calcium tube between the two.

Instead of weighing the substance in a boat, it may just as well be placed in a bulb-tube. In case the substance to be analyzed is likely to absorb oxygen when heated in air it should be ignited in a current of dry carbonic acid.

Indirect separation of Calcium from Strontium.

Precipitate the two metals as carbonates, — see Carbonate of Calcium, — weigh the mixed precipitate and call its weight *W*. Afterwards ignite the precipitate at a moderate white heat, until all the carbonic acid has been driven out from both the carbonates, and weigh the residual oxides. The difference between the two weights will give the weight of the carbonic acid. Calculate this carbonic acid as if the mixed carbonates were really nothing but carbonate of strontium, thus,

$$\begin{array}{l} \text{Molec. wt.} \\ \text{of } \text{CO}_2 \\ 44 \end{array} : \begin{array}{l} \text{Molec. wt. of} \\ \text{SrO, CO}_2 \\ 147.5 \end{array} = \begin{array}{l} \text{Weight of} \\ \text{CO}_2 \\ \text{found} \end{array} : x \left(= \begin{array}{l} \text{Weight of} \\ \text{supposed} \\ \text{SrO, CO}_2 \end{array} \right)$$

The difference ($x-W$) between the weight of the supposed carbonate of strontium, and that of the mixed carbonates actually found, is proportional to the quantity of carbonate of calcium in the mixture, so that the weight of the last named salt may be obtained by the proportion:

$$\begin{array}{l} \text{Difference between} \\ \text{the molec. weights} \\ \text{SrO, CO}_2 \text{ and CaO, CO}_2 \\ 47.5 \end{array} : \begin{array}{l} \text{Molec. wt.} \\ \text{CaO, CO}_2 = (x-W) : y \left(= \begin{array}{l} \text{Wt. of} \\ \text{CaO, CO}_2 \\ \text{in the} \\ \text{mixed carb's} \end{array} \right)$$

In short, multiply the carbonic acid found by $147.5 \div 44$ ($= 3.3534$), deduct from the product the weight of the carbonates, and multiply the difference by $100 \div 47.5$ ($= 2.10526$). The product* will express the weight of the carbonate of calcium. The difference between this weight and that of the mixed carbonates will give the weight of the carbonate of strontium. The process gives good results unless the quantity of one or the other of the metals in the mixture is too minute.

Precautions. The mixed precipitate should be thrown down from hot solutions. During the process of ignition the agglomerated mass should be turned over now and then in the platinum crucible, and pressed down carefully against the hot metal until, after repeated ignitions, its weight remains constant. If the operator prefer, the carbonic acid may be estimated by fusing with borax glass (see below), but a moderate white heat such as may readily be obtained by a blast lamp is sufficient for the purpose. (Schaffgotsch, *Pogg. Ann.*, 113. 615).

Method B. By ignition with a solid, non-volatile acid, or acid salt. By this method, carbonic acid can be separated from all the bases which form anhydrous carbonates, and its amount determined with great accuracy. The principle is applied also in organic analysis, for expelling carbonic acid from the carbonates of K, Na, Ca, Ba and Sr, in cases where either of these compounds is formed during the combustion of the organic substances. The same principle is involved, moreover, in the method of estimating boric acid indirectly by igniting a carbonate with borax glass, as has been explained under Boracic Acid. It is applied also to the indirect separation of barium from strontium or calcium, and of strontium from calcium, as will be explained immediately.

1. *Fusion with Borax-glass.* Fuse a quantity of borax-glass (see *biBorate of Sodium*) in a weighed platinum crucible, place the crucible with its contents in a dessicator to cool, and weigh when cold. Place in the crucible a quantity of the carbonate to be analyzed, and again weigh so that both the weight of the carbonate and that of the borax may be known. The carbonate should be perfectly dry, and should weigh about a quarter as much as the borax glass. Gradually heat the mixture to redness, and keep it at that temperature until the contents of the crucible are in a state of tranquil

fusion and no more bubbles of carbonic acid escape from the molten liquid. No heed need be taken of a few persistent bubbles of gas which are liable to remain in the liquid. Again place the crucible in the dessicator and weigh it, with its contents, when cold. The loss of weight represents the amount of carbonic acid in the substance analyzed. The mixture must not be ignited over a blast lamp, lest a certain amount of borax glass be lost through volatilization. (Schaffgotsch).

To separate barium from strontium or from calcium, by the indirect method, throw the two metals down together as carbonates, see Carbonate of Barium (insolubility of), and note the weight of the mixed precipitate. Then expel the carbonic acid by fusing with borax-glass, and note the weight of the acid. The proportion of the different metals in the mixed precipitate may be calculated as follows. Compare the method by simple ignition, above.

To separate Ba from Sr:—Calculate the carbonic acid as if it belonged to strontium, thus:—

$$\frac{\text{Molec. wt. of CO}_2}{44} : \frac{\text{Molec. wt. of SrO}_2 \cdot \text{CO}_2}{147.5} = \frac{\text{Wt. of CO}_2 \text{ found}}{\text{Weight of supposed SrO}_2 \cdot \text{CO}_2} : x$$

and subtract from this supposititious weight the weight of the mixed carbonates (W) found. The number $(x - W)$ thus obtained, is proportional to the quantity of carbonate of barium in the mixture; hence the weight of the barium salt may be obtained by the proportion.

$$\frac{\text{Diff. between molec. wts. of SrO}_2 \cdot \text{CO}_2 \text{ and CaO}_2 \cdot \text{CO}_2}{49.5} : \frac{\text{Molec. wt. of BaO}_2 \cdot \text{CO}_2}{197} = \frac{(x - W)}{\text{Wt. of BaO}_2 \cdot \text{CO}_2 \text{ in mixed carbonates}} : y$$

In short, multiply the carbonic acid found by $147.5 \div 44$ ($= 3.3534$), deduct from the product the weight of the mixed carbonates, and multiply the difference with $197 \div 49.5$ ($= 4.4246$). The product will express the weight of the carbonate of barium. The difference between this weight and that of the mixed carbonates will give the weight of the carbonate of strontium.

To separate Ba from Ca, proceed in a similar way, calculating the carbonic acid, at first, as if it were all carbonate of calcium.

2. *Fusion with Bichromate of Potassium.* Select a combustion tube of hard glass 50 or 60 c. m. long, and bend it in such manner that it shall be very slightly U-shaped at the middle, while the two ends remain horizontal. Fasten to one end of this tube a pipe closed with a copper stop-cock and connected with a permanent set of potash and chloride of calcium tubes, suitable for removing carbonic acid and water from the air. To the other end of the combustion tube attach a weighed chloride of calcium tube and a set of potash bulbs, or a soda-lime tube, precisely as in the estimation of Carbon, and to the potash bulbs attach an aspirator. It is well to attach a small supplementary weighed chloride of calcium tube to

the potash bulbs, and also to interpose an unweighed chloride of calcium tube between the absorption tubes and the aspirator, to guard against the aqueous vapor which may arise from the latter. — Place in the combustion tube from 30 to 60 grms. of bichromate of potassium, which has been fused just before the experiment, together with from 1 to 3 grms. of the carbonate to be analyzed, and place a loose plug of ignited asbestos in front of the mixture. Carbonates of the alkali metals may be introduced in the form of fragments, but most of the other insoluble carbonates must be finely powdered and mixed with the bichromate. After the mixture has been placed in the combustion tube, and the latter connected with the absorption tubes, heat the mixture of bichromate and substance, and allow a slow stream of water to flow from the aspirator, so that a current of air shall be drawn through the apparatus. The evolution of carbonic acid begins as soon as the bichromate melts, and it admits of being easily regulated. The operation is finished when the whole of the mixture is seen to be in a state of tranquil fusion. The increase in weight of the potash bulbs or soda-lime tube, gives the weight of the carbonic acid, and that of the chloride of calcium tube the weight of the water in the substance analyzed, in case any water was present. The presence of sulphites or hyposulphites, or of sulphides or oxysulphides of the alkali or alkaline-earthly metals, does no harm, but the substance analyzed must of course be free from carbonaceous matters.

The process may be applied not only to the estimation of carbonic acid for its own sake, but for determining the alkalimetric value of the carbonates of potassium and sodium. (See below, under "Expulsion of Carbonic Acid by Acids"). (Persoz, *Comptes Rendus*, 53. 239).

3. In the analysis of organic compounds which contain an alkali-metal or a metal of one of the alkaline earths, mix the substance with a quantity of boracic or antimonious acid, or with phosphate of copper, before placing it in the combustion tube. (Compare Carbon).

Method C. Expulsion by acids at the ordinary temperature. By this method carbonic acid may be separated from all bases, without exception. The evolved gas may then be measured as such, or determined as loss, or estimated indirectly from the weight or by the analysis of the residue, or, better, it may be determined by absorption in an alkali in accordance with Principle I.

1. *By Loss.* The earlier chemists were content to throw a weighed quantity of the carbonate to be analyzed into 3 or 4 times as much chlorhydric, nitric, or sulphuric acid contained in a tall cylinder, and counterpoised upon a balance. When the effervescence ceased, the increase of weight on the part of the cylinder was noted, and the difference between that quantity and the weight of carbonate taken

was reckoned as carbonic acid. Care was taken to avoid loss by spirting, and that the operation should proceed rather rapidly, so that as little acid as might be should be lost by evaporation. The acid usually employed was either nitric acid of 1.15 sp. gr., or a mixture of strong chlorhydric acid with an equal bulk of water. (Pfaff, *Handbuch analyt. Chem.*, 1824, 1. 505; 2. 18). Of late years, however, the method has been greatly perfected by the invention of apparatus specially arranged so as to avoid the risk of loss by evaporation or transportation of the solvent acid.

A great many different forms of the apparatus have been devised by chemists, see, for example, *Mohr's Titrimethode*, 1855, p. 122, and *Fresenius's Quantitative Analysis*, 1865, p. 300. The essential features of the apparatus are, 1st, a small glass flask, in which to place the substance to be analyzed, and in which, at the proper moment, to mix the substance and the acid by which it is to be decomposed; 2d, a tube or flask to hold this acid and keep it away from the carbonate until the time when the operator sees fit to mix the materials; 3d, a chloride of calcium tube, or other apparatus, for drying the gas evolved by the action of the acid on the carbonate, so that nothing but absolutely dry carbonic acid can escape from the flask.

A simple form of the apparatus may be made as follows: Choose a small, wide-mouthed flask, and fit to it a soft cork or rubber stopper with two perforations. Pass the stem of a chloride of calcium tube through one hole of the cork, and insert in the other hole a narrow glass tube bent at a right angle and reaching nearly to the bottom of the flask. Make a small bottle, like a homœopathic phial, from a piece of tolerably wide glass tubing, by closing one end of the tube at the lamp, and pressing the softened glass flat, so that the short tube, or bottle, may be made to stand upright. This little bottle must be capable of passing readily through the neck of the flask. To the top of the bottle tie a thread, or better, a piece of fine platinum wire, a little longer than the flask is high.

The actual analysis is performed as follows: Place in the flask a weighed quantity of the carbonate to be analyzed, and fill the little bottle two-thirds full of acid. By means of the thread or wire lower the bottle carefully into the flask, leaving the upper end of the thread projecting from the flask. Press the cork into the neck of the flask so that the thread or wire may be held firmly between the cork and the glass, taking care not to spill any of the acid out of the bottle. Plug the outer end of the plain glass tube with a small ball of wax, or better, with a bit of rubber tubing closed with a short piece of glass rod, and leave the apparatus at rest during 15 or 20 minutes in a room of tolerably constant temperature before weigh-

ing or counterpoising it. Then hold the flask in an inclined position, so that the acid in the bottle may run out, little by little, upon the carbonate. The carbonic acid set free is dried more or less completely as it passes out through the chloride of calcium tube. — After the evolution of gas has ceased, remove the stopper from the narrow glass tube, attach to the latter an unweighed chloride of calcium tube, connect the permanent chloride of calcium tube with an aspirator, and draw a quantity of air through the flask. After all the gaseous contents of the flask have been swept out by the current of air, there still remains a certain quantity of carbonic acid dissolved in the liquid at the bottom of the flask. In order to remove this dissolved gas, disconnect the flask from the temporary chloride of calcium tube and aspirator, plug the narrow glass tube, and slowly heat the contents of the flask to incipient boiling. Then remove the plug, re-attach the chloride of calcium tube and the aspirator, and again draw a quantity of air through the flask. When all the carbonic acid has been swept out, disconnect the flask from the aspirator and temporary drying tube, plug the narrow glass tube, allow the flask to cool for half an hour in the room of constant temperature, replace it upon the balance and determine how much less it weighs than at first. The loss of weight represents the carbonic acid in the substance analyzed. — Good results are sometimes obtained in this way, but it is nevertheless a matter of common experience that the loss of weight of the apparatus cannot be counted as carbonic acid with certainty. If the dilute acid liquor in the flask be heated long enough and strongly enough to expel all the carbonic acid which is dissolved by it, some aqueous vapor will be driven out of the apparatus also, and lost. In most cases, where good results are obtained, the agreement is really due to the compensation of opposite errors, as may be seen by trying the experiment of repeatedly heating the flask of the apparatus and sucking air through it. If the suction be continued just long enough, the diminished weight of the apparatus will exactly correspond to the carbonic acid that was contained in the substance, but further exhaustion of the air will diminish the weight of the apparatus, not by complete removal of the carbonic acid, but by loss of aqueous vapor, which easily escapes through the desiccating material. By continued working on a carbonate of known composition, one may soon learn how long to exhaust in order to bring about the proper loss, but where the analyst is out of practice an error of 1 or 2 per cent is not unlikely to happen, and the process itself furnishes no means of judging when it will give a correct result. (S. W. Johnson, *Amer. Journ. Sci.*, 1869, 48. 111). A far better method is to charge the apparatus with carbonic acid gas in the first place, and to weigh

it full of carbonic acid as soon as the disengagement of gas has ceased. See below, *Johnson's modification*.

Choice of the decomposing acid. Usually the acid employed for decomposing the carbonate is either sulphuric, nitric, chlorhydric or oxalic. When the substance analyzed contains a fluoride, however, some weak, non-volatile acid, such as tartaric or citric acid must be employed to set free the carbonic acid, for if either of the mineral acids were used, some fluorhydric acid would be evolved. Sulphuric acid is to be preferred for the treatment of the carbonates of all those metals which form soluble sulphates, but is unfit for decomposing the carbonates of metals which form insoluble compounds with sulphuric acid, for the insoluble layer of sulphate formed by the action of the first portions of the acid would cover over a part of the carbonate, and prevent the acid from coming in contact with it. Nitric, or in some instances chlorhydric, acid must therefore often be substituted for the sulphuric acid.

When chlorhydric acid is used to decompose a carbonate, or in case the latter is contaminated with a chloride, the escaping carbonic acid should be made to pass through a tube filled with some substance, like anhydrous sulphate of copper, which has power to retain both water and chlorhydric acid. To prepare the sulphate of copper, boil fragments of pumice stone in a concentrated aqueous solution of blue-vitriol, and dry and heat the stone until the copper salt is completely dehydrated and has become white. A U-tube about 8 c. m. high and 1 c. m. bore filled with the sulphate will usually be found sufficiently large; it may be used as long as a third of its contents remain uncolored. (Stolba, *Dingler's polytech. Journ.*, 164. 128). In case a carbonate fit to be treated with sulphuric acid happens to be contaminated with a chloride, the risk of evolving chlorhydric acid may be avoided by mixing the weighed carbonate with a quantity of a solution of sulphate of silver before adding the acid. So too, if the carbonate contains a sulphite or a sulphide, these salts may be oxidized by treating the weighed carbonate with a solution of yellow chromate of potassium before adding the acid.

In some cases it will be found advantageous to determine the metallic base of the carbonate, by Alkalimetry, in the solution left in the flask. In this event, mix the weighed carbonate with a weighed quantity of crystallized oxalic acid more than sufficient to decompose the whole of the carbonate, charge the tube with water, and at the proper time pour the water upon the mixture of acid and carbonate. After all the carbonic acid has been expelled from the flask, determine how much of the oxalic acid has been left free by titrating with an alkaline solution of known strength (see Alkalimetry). Instead of using solid oxalic acid, the tube might be charged with tolerably

strong standard sulphuric, nitric, or chlorhydric acid. As thus modified, the process is peculiarly useful for determining the relative proportions of carbonic acid and base in unweighed quantities of moist, recently precipitated carbonates, and in carbonates which cannot be dried without suffering decomposition. (Stolba, *Journ. prakt. Chem.*, 97. 312).

Application to Alkalimetry. The method now in question is sometimes employed as an alkalimetric process for determining the value of commercial carbonates of sodium or potassium in cases where the carbonates are strongly colored. For this alkalimetric determination a form of apparatus devised by Fresenius & Will is usually employed. Though similar in principle to the apparatus above described, the alkalimeter of these chemists is peculiar in some of its details. It may be readily made as follows:—Select two small, light Berlin flasks. Fit to each flask a cork or caoutchouc stopper, and bore two holes in each of the corks. Place the flasks upon a table, side by side, so that they shall almost, but not quite, touch one another. Call the flask at the left hand L, and the other R. Bend a glass tube at two right angles, in such manner that one leg of the tube may pass into the flask L, and the other into the flask R. Push one leg of the bent tube through one of the corks and the other through the other. Cut off one leg of the tube just below the cork of the flask L, but leave the other leg long enough to reach almost to the bottom of the flask R. Through the second hole of the cork in L pass a straight tube, open at both ends, long enough to reach almost to the bottom of the flask, and through the corresponding hole of the cork in R push a similar, but shorter, tube long enough to project a few m. m. below the cork. — The size of the flasks must be determined by the capacity and delicacy of the balance at the disposal of the operator. If the apparatus is to be weighed upon a delicate chemical balance, it may be made so light that when fully charged with acid it need not weigh more than 70 or 80 grammes; but as a general rule it will be found more convenient to use somewhat larger flasks and to operate upon a coarser balance.

To use the apparatus, plug the upright tube in the flask L, as directed in a previous paragraph; pour the weighed carbonate into L, and add to it enough water to fill about a third of the flask. Pour enough strong sulphuric acid into the other flask, R, to half fill it; re-place the corks and push them tightly into the mouths of the flasks. Let the apparatus stand 15 or 20 minutes in a room of tolerably constant temperature, and then counterpoise it upon a balance. Attach a piece of caoutchouc tubing to the upright tube in R, and proceed to test the tightness of the apparatus. To this end, suck out a small quantity of air from the flask R, so that a few bubbles of air may escape from L into R, through the sulphuric

acid, to supply the partial vacuum which has been created in R. Then remove the lips from the caoutchouc tube, and suffer the external air to enter R. If the apparatus is tight, some sulphuric acid will be pressed up towards L, in the bent glass tube, and will remain stationary in the tube. Watch the column of sulphuric acid for a few minutes to see that it does not sink back into R, and then suck a quantity of air from R, somewhat larger than before. On removing the lips from the caoutchouc tube, a portion of the sulphuric acid in R is forced over into L, and decomposes a corresponding quantity of the carbonate therein contained. The carbonic acid set free passes through the sulphuric acid in R, and is thereby dried before escaping into the air through the open, upright tube. As soon as the effervescence in L slackens, suck out more air from R, so that a new quantity of sulphuric acid may be forced over into L, and repeat the operation at intervals until the whole of the carbonate is decomposed. When the effervescence has entirely ceased, force over a comparatively large quantity of the sulphuric acid into L, so that the contents of that flask may be considerably heated. After a few moments, remove the plug from the upright tube in L, attach to the tube a chloride of calcium tube, and by means of the caoutchouc tube at the other flask, suck air through the apparatus until this air no longer tastes of carbonic acid. Let the apparatus stand at rest in the room of constant temperature for 2 or 3 hours, replace it upon the balance, and bring the latter into equilibrium by means of weights. The sum of the weights added indicates the amount of carbonic acid which has been expelled from the substance analyzed.

$$\frac{\text{Molec. wt. of } \text{CO}_2}{\text{Molec. wt. of } \text{Na}_2\text{CO}_3} = \frac{\text{Wt. of } \text{CO}_2 \text{ found}}{\text{Wt. of } \text{Na}_2\text{CO}_3 \text{ in sample}}$$

Tolerably accurate results may be obtained by this method, unless the proportion of carbonic acid in the substance analyzed is very small.

To fit the apparatus just described for the analysis of lime-stone and the carbonates of other metals forming insoluble sulphates, replace the straight, upright tube in L by a tube which has been blown to a somewhat capacious bulb near the top, and drawn to a fine point at the lower end. The apparatus is charged as before with the exception that the bulb-tube is filled with dilute nitric acid, and that at the start the lower part of the tube is not pushed so deep into the flask as in the other case. Care must be taken that the point of the bulb-tube does not touch the water in L until after the apparatus has been counterpoised on the balance.

Like the straight tube of the apparatus previously described, the bulb-tube must be closed at the top with a moveable plug so that none of the nitric acid can flow out until the plug is

loosened. The quantity of nitric acid taken must be more than sufficient to decompose the whole of the carbonate.

In case the metallic base of the carbonate is to be determined as well as the carbonic acid (see above, p. 82), a measured quantity of standard acid must be introduced into the bulb-tube. To this end, hold the tube point upwards, warm the point over a lamp, and touch it with a bit of tallow in such manner that a little of the tallow may solidify in the tube, and close it water tight. Then invert the tube, fill it through the upper opening with the acid, measured from a Mohr's burette with fine point, plug the upper opening in the usual way, and heat the point of the tube gently until the tallow is melted.

After the apparatus has been counterpoised carefully push down the bulb-tube until it touches the water, and at intervals loosen the plug so that small quantities of the nitric acid may flow out upon the carbonate. As soon as the carbonate has been completely decomposed, suck air through the apparatus as before, and finally heat the contents of the flask L to incipient boiling, in order to set free the last traces of the gas.

Application to Acidimetry. The volatility of carbonic acid has been made the basis, not only of a process of alkalimetry, as just described, but of a method of acidimetry as well. It is in fact easy to estimate the strength of any sample of acid, by weighing the carbonic acid set free from bicarbonate of sodium by the acid in question. The operation is as follows:—In the flask L of the apparatus just described, weigh out a quantity of the acid to be examined, and if it be concentrated, dilute it with water. In either case, the fluid should fill about a third of the flask. Fill a small glass tube compactly with bicarbonate of sodium or of potassium. Tie a thread to the tube and hang it in the flask L by pressing the thread between the cork and the neck of the flask. The quantity of bicarbonate taken must be more than sufficient to saturate the acid in the flask; the salt must be free from monocarbonate, but the presence of chloride or sulphate, etc., of sodium, does no harm. In other respects the apparatus is charged in the manner already described in the case where the upright tube in L is straight. After the apparatus has been counterpoised, loosen the cork of the flask L, so that the thread may slacken and let the tube of bicarbonate fall to the bottom of the flask, and at the same instant replace the cork as tightly as possible. Carbonic acid is given off violently at first, then for some time at a uniform rate, afterwards slowly until the evolution ceases. When no more gas is evolved, put the flask L in water of from 50° to 55° C, so hot that the finger cannot long be held in it, and when the renewed evolution of gas thus occasioned has ceased, suck air through the appa-

ratus, as before. When practicable, enough acid should be taken to set free a gramme or two of carbonic acid.

In *Johnson's Modification* of the foregoing method of estimating carbonic acid, the apparatus is weighed full of carbonic acid, both before and after the experiment, so that there is no need of sucking out any gas from the flask. The desiccating material has consequently to dry only as much gas as is yielded by the substance subjected to analysis. The process thus modified is much better than before, and is decidedly to be preferred to the old method in all cases where the substance to be examined dissolves freely and completely in cold acid.

The apparatus may consist of a light, wide-mouthed flask or bottle, from 3 to 3.5 c. m. wide by 6 c. m. high, closed with a caoutchouc stopper, to perforations in which are fitted an upright chloride of calcium tube and the bent end of a tolerably capacious bulb-tube, which serves as a reservoir of acid. A good chloride of calcium tube may be made by blowing two oblong bulbs, each 2.25 c. m. broad, on a glass tube. When finished, the tube may be about 10 c. m. long. The lower bulb is filled with cotton, the upper with small fragments of porous chloride of calcium, and the top of the tube is closed with a rubber connector, plugged with a bit of glass rod. The acid reservoir may be made by blowing an oblong bulb about 3 c. m. wide by 5 c. m. or more long, on a tube of about 7 m. m. internal diameter, and bending the tube in such manner that while the bottom of the bulb, or rather the bent tube immediately adjacent to the bottom of the bulb, shall rest upon the table, close beside the flask, there shall be a short, bent delivery tube to connect the upper, narrower end of the bulb with the rubber stopper, and at the other end of the bulb, a tube pointing upwards and reaching to the level of the top of the flask; this longer tube serves for the introduction of carbonic acid at the beginning of the experiment. The extremity of the upper or delivery tube reaches fairly through the rubber stopper; it is ground off obliquely, so that no drop of liquid can be held in it. At the top of the tube for introducing carbonic acid there is a short rubber connector with a glass-rod plug.

The actual analysis of carbonate of calcium, for example, is made as follows;—Put from half a grm. to a grm. of the substance, best in the form of small fragments, into the flask. Fill the bulbous acid reservoir nearly full of chlorhydric acid of 1.1 sp. gr. Fit the rubber stopper, with its appurtenances, tightly into the mouth of the flask; remove the glass-rod plugs, connect the upright tube with a self-regulating carbonic acid generator, and pass a rather rapid stream of washed carbonic acid through the apparatus during 15 minutes, or until the acid in the bulb is saturated and all the air in the flask has been displaced by the

gas. Then plug the top of the chloride of calcium tube, disconnect the apparatus from the source of carbonic acid, plug the upright tube and immediately weigh. Take care to handle the apparatus carefully so that its temperature shall not be changed by the warmth of the hands. After weighing, loosen the plug of the chloride of calcium tube, and, holding the flask by a wooden clamp, incline it so that the acid may flow over upon the carbonate. The decomposition should proceed slowly, so that the escaping gas may be thoroughly dried. As soon as the whole of the carbonate has dissolved, replace the plug in the chloride of calcium tube and weigh the apparatus. — All the joints of the apparatus must be gas-tight; should there be any leak it will be made evident at the final weighing, by a slow but steady loss of weight as the apparatus stands upon the balance. If all the joints are sufficiently tight, the weight will remain the same for at least 15 minutes. Since the temperature of the flask usually rises a little during the solution of the carbonate, it is best, after the decomposition of the latter is completed, to plug the chloride of calcium tube and leave the apparatus at rest for 15 minutes; then connect with the carbonic acid generator as before, and pass dried carbonic acid for a minute before weighing.

When properly executed, the process gives extremely accurate results. It is essential, however, that the operation and the weighings be conducted in an apartment not liable to sudden changes of temperature. A slight change of temperature or of atmospheric pressure between the two weighings greatly impairs the results, or renders them worthless.

In the case of alkali-metals which absorb carbonic acid gas, a small bottle of thick glass and wider mouth should be used in place of the flask above described. The stopper of this bottle should have three holes, the third to carry a narrow tube 3 or 4 inches long enlarged below to a small bulb, to hold the carbonate. This bulb must be so thin that on pushing down the tube within the bottle, it shall be easily crushed to pieces against the bottom of the latter. The carbonate is weighed into the bulb-tube, the latter is wiped clean, corked and fixed in the rubber stopper. The apparatus is filled with carbonic acid and weighed. The bulb is then broken and the process proceeded with precisely as above described. (*S. W. Johnson, Amer. Journ. Sci.*, 1869, 48, 111, and the American edition of *Fresenius's Quant. Anal.*, New York, 1870, p. 202. The apparatus is figured in both places).

2. *By measuring the carbonic acid gas.* The process is applied to the determination of carbonic acid in soils, manures, mortars, marls, bone-black and the like. Also in the analysis of mineral waters and blood. Like the foregoing method it may be used for estimating the alkalimetric value of the carbonates of potas-

sium and sodium. For the determination of small quantities of carbonic acid, the method by measuring is thought by some chemists to be preferable to either of the other methods.

As described by Pfaff (*Handbuch analyt. Chem.*, 1824, 1. 505; 2. pp. 18, 77), the process consisted in putting small fragments of the carbonate into a graduated tube charged with chlorhydric acid, and placed, full of mercury, in a mercury trough. In case the substance to be analyzed was in the state of powder, it was done up to little pellets in paper which had been previously leached with chlorhydric acid. Due allowance was made for temperature and barometric pressure. — The more modern methods are as follows:—

A. *Method of Schulze.* This method may be used for estimating the proportion of carbonate of calcium, or any other carbonate, in rocks, soils and manures, and in general for all cases where the substance to be analyzed is bulky, the volume of gas to be evolved is large, or the evolution of gas attended with frothing. The apparatus required consists of two glass bottles, one for decomposing the carbonate and the other for collecting the gas set free, a tubulated retort to hold the acid by which the decomposition of the carbonate is to be effected and a small metallic water-tank to cool the collecting bottle. — Heat the upper part of the neck of a small tubulated retort in the flame of a blast lamp, and bend the softened glass in such manner that the neck of the retort shall point almost perpendicularly downwards. Obtain a stout, two-necked bottle of about 350 c. capacity, for the decomposing jar, and an aspirator-flask of 1 or 1.5 litres capacity, for the collecting bottle. One of the orifices of the decomposing bottle must be tolerably wide, and thick and strong in glass, while the other opening is made in the form of a plain projecting tube. To the upper orifice of the collecting bottle, and to the wider orifice of the decomposing bottle, fit perforated ground glass stoppers. Cement the neck of the bent retort into the perforation of the stopper of the decomposing bottle, and a short, straight glass tube into the perforation of the stopper of the collecting bottle. Connect the two bottles by means of a caoutchouc tube, one end of which is tied to the projecting neck of the decomposing bottle and the other to the straight glass tube in the stopper of the collecting bottle. Place the collecting bottle in a zinc cylinder as tall as the bottle and provided with a lateral opening near the bottom corresponding to the orifice in the side of the bottle. Close the side opening of the bottle with a cork carrying a glass tube bent at a right angle, the longer limb of which projects upwards a little higher than the top of the bottle. The bore of this tube should be about 4 or 5 m. m. in diameter excepting the point, which is narrowed to 2 m. m. By means of a short piece of caoutchouc tubing tied to the lateral tubulures of the col-

lecting bottle and the zinc cylinder, the latter is made tight; it is then filled with water. The collecting bottle is also filled with water, together with enough fatty oil to form a thin layer upon the surface of the water.

In an actual analysis, a weighed quantity of the substance, such as marl or lime stone, to be examined, is placed in the decomposing bottle. The retort is three-fourths filled with dilute chlorhydric acid of 1.05 or 1.07 sp. gr., and the stopper to which the retort is cemented is carefully greased and inserted in the neck of the decomposing bottle. The apparatus is left in a room of tolerably constant temperature until the retort and decomposing jar, as well as the water in the zinc cylinder, have acquired the temperature of the air of the apartment. The stopper of the collecting jar is then smeared with tallow and inserted in its place, and the glass tube in the side orifice of the collecting jar is turned perpendicularly downwards. A beaker is placed beneath this tube to catch the water which flows from the collecting bottle. If the apparatus is tight, only a small quantity of water will flow from the bottle when the tube is turned down. Incline the decomposing bottle to such an extent that acid may slowly flow from the retort upon the carbonate in the decomposing bottle. The carbonic acid evolved will pass over into the collecting jar, while water will flow out of the latter into the beaker to make room for the gas. As soon as the decomposition is finished, prop up the beaker beneath the tube of the collecting jar so that the mouth of the tube shall be immersed in the water, and set the decomposing bottle in a jar of water of the same temperature as that in the zinc cylinder. As soon as all parts of the apparatus have acquired a common temperature, remove the beaker of water, turn the water delivery tube of the collecting jar perpendicularly upwards, take out the stopper of the retort for a moment, again turn the water tube downwards, and collect by itself the small quantity of water which flows from the collecting jar. Measure this water and note the quantity. Measure also the water which was previously collected in the beaker. The difference between the two quantities will give the volume of the carbonic acid under the existing conditions of temperature and barometric pressure,—subject also to a correction for the tension of aqueous vapor at the temperature in question.

The weight of the carbonic acid obtained may readily be calculated from the volume, by referring to the known specific gravities of carbonic acid and air, or it may be determined still more simply by decomposing a known quantity of pure carbonate of calcium in the apparatus. The weight of the volume of carbonic acid obtained from the pure carbonate being known, *a priori*, this volume may be directly compared with any other volume of the gas. By operating in this way, moreover, several slight sources

of error incidental to the method of experimenting may be avoided. It is not even necessary to use pure carbonate of calcium for the comparative experiment;—almost any sample of marble whose percentage of carbonic acid has been carefully determined will answer as well. After the value of a marble has once been determined for this purpose a considerable store of the material had better be kept on hand.

The process is simple and is said to yield exceedingly accurate results.

Precautions. The oil employed to cover the water in the collecting bottle must be fresh and indisposed to rancidity. In practice it is found that the oil absorbs carbonic acid so slowly that the loss of gas from this cause during the time required for an experiment is scarcely appreciable. — Care must be taken not to warm the collecting bottle with the hand when the stopper is placed in the bottle. — The chlorhydric acid employed had better be of 1.05 or 1.07 sp. gr., since a stronger acid would affect the tension of the aqueous vapor in the apparatus. — The control experiment with marble or pure carbonate of calcium is of special value in cases,—such as the analysis of artificial manures, soils, peat-ashes, and the like,—where the proportion of carbonic acid in the substance is so small that a comparatively large quantity of liquid has to be mixed with the substance in order that the carbonate contained in it may be wholly decomposed. The liquid of course retains a quantity of carbonic acid in solution, but by repeating the experiment with marble which has been mixed with a quantity of inert sand and as much water as was used in analyzing the substance, this source of error may be so much diminished that accurate results may still be obtained with materials containing no more than 0.5 per cent of carbonate of calcium. In operating with these earthy materials, the decomposing jar must be freely shaken in order that carbonic acid may escape, and the control experiment with the marble must be subjected to the same amount of agitation. The quantity of carbonic acid retained by the water can, for that matter, be determined for any special series of experiments and allowed for, or the carbonic acid may be displaced from the water by means of hydrogen. To this end mix with the carbonate to be analyzed a weighed quantity of zinc powder, each gramme of which has been found capable, by previous experiments, of evolving a certain number of c. c. of hydrogen, when treated with chlorhydric acid. On pouring chlorhydric acid from the retort into the decomposing flask the carbonate will first be decomposed before much of the zinc is acted upon, so that hydrogen will continue to be set free in the liquid long after the carbonate has been completely decomposed. If enough zinc be used, the hydrogen will sweep forward into the collecting jar almost all the carbonic acid which would otherwise have been retained by

the liquor. The volume of hydrogen equivalent to the zinc employed is subtracted from the measured volume of carbonic acid and hydrogen. — This method of displacement by hydrogen becomes somewhat more complicated in certain cases, particularly in presence of nitric and oxalic acids, ferric oxide and other substances capable of preventing the evolution of hydrogen. Soils, for example, not only contain substances which combine with and retain nascent hydrogen, but the zinc powder becomes so completely enveloped by the earthy particles that a long time is required in order that the whole of the metal may dissolve. In order to displace carbonic acid by hydrogen therefore, in analyzing soils, manures and the like, it is necessary to treat the zinc with acid in a special vessel and to lead the free hydrogen through the solution of carbonic acid.

A convenient way of arranging the apparatus is to interpose a second two-necked bottle between the decomposing and collecting bottles. The orifices of this second bottle are closed with perforated caoutchouc stoppers, through one of which a glass tube passes to the bottom of the bottle. The upper end of this glass tube is connected, by means of a caoutchouc tube, with the outlet of the decomposing bottle. A short, straight glass tube placed in the perforation of the other stopper is connected, by means of another flexible tube, with the top of the collecting bottle. The substance to be analyzed is placed in the new two-necked bottle together with a test tube full of chlorhydric acid of 1.05 sp. gr., while the weighed zinc powder is placed in the old decomposing bottle. After the apparatus has been proved to be tight, the bottle which contains the carbonate is inclined so that the acid in the test tube may flow out into the bottle, and, finally, acid is made to flow from the retort upon the zinc powder. When no more hydrogen is evolved, lift the long tube in the new two-necked bottle, out of the liquid, bring the apparatus to a common temperature and measure the water in the beaker as before. (F. Schulze, *Zeitsch. analyt. Chem.*, 1863, **2**, 289).

B. Method of L. Meyer, for determining carbonic acid in mineral waters and in blood. In order to remove carbonic acid (and other gases) from a liquid, Meyer employs a modification of the apparatus of Ludwig¹ based upon the principle of the Torricellian vacuum.

This apparatus may be roughly described as follows:—A stout glass vessel of about 700 c. c. capacity, filled with mercury, is attached to a long vertical tube, also full of mercury, in such manner that on allowing mercury to flow from the bottom of the tube a vacuum can be formed

¹ See Setchenow, *Wien. Akad. Bericht.*, **36**, 293; Schœffler, *ibid.*, **41**, 589, and Heidenhain, *Zeitsch. analyt. Chem.*, 1863, **2**, 120.

in the vessel. The flask which contains the mineral water is connected with the glass vessel by means of a flexible tube closed with a screw compressor, so that on opening the latter the gases contained in the water will be given off to supply the vacuum. As soon as any considerable quantity of gas has escaped from the water the compression cock is again closed and the gas forced over into a collecting tube, standing in a pneumatic trough beside the vacuum jar, by pouring mercury into the latter. The vacuum is then re-established as before, and the compression cock again opened so that a new quantity of carbonic acid may exhale from the water; the glass vessel is thus alternately filled and emptied of mercury as long as any gas continues to escape from the water. The flask which contains the water is heated after a while to facilitate the escape of carbonic acid, and at a certain stage of the process tartaric acid is added to the water, in order to expel any carbonic acid which may have been previously held in combination by a base.

The proportion of carbonic acid in the gas thus set free is then determined by the usual gasometric method described under Hydrate of Potassium.

For details of the method employed for collecting and analyzing the blood of animals the reader is referred to the article of Heidenhain (*Zeitsch. analyt. Chem.*, 1863, 2, 122). With mineral waters Meyer proceeds as follows:—The water is collected at the spring in ordinary bolt-heads of about 1 litre capacity, whose throats have been drawn out to the width of about 1 c. m. The flasks may be closed securely with thick caoutchouc tubing which has been freed from adhering sulphur by boiling with soda lye or sulphhydrate of ammonium, and afterwards soaked in fat upon a water bath. The walls of this tubing should be at least 5 m. m. thick; after the treatment with fat the tubing should be washed first with alcohol, then with water, and dried. — Before forcing the tubing over the neck of the flask the latter should be smeared with a hot mixture of fat and unvulcanized caoutchouc. The rubber tube is then tied tightly to the glass with fine, soft iron wire, and the flask sunk in the water of the spring. When a sufficient quantity of water has run into the flask, the caoutchouc tube is closed under water with a screw compressor, a glass rod smeared with the mixture of fat and rubber is pushed into the outer end of the tube and the tube is tied to the rod with wire, as before. In flasks thus closed, mineral water can be kept for days or weeks without loss of gas. — In order to attach one of these flasks to the vacuum apparatus, take out the glass rod and put in its place a bulb-tube about 10 c. m. long, of 20 or 30 c. c. capacity, attach a second caoutchouc connector to the other end of the bulb-tube, and tie it to the orifice of the glass vessel in which the vacuum is produced. This bulb-tube serves to

receive the water which is expelled from the flask through the expansion of the liquid by heat, and also for the reception of the tartaric acid which is added to expel the combined carbonic acid. After the water flask has been connected with the glass vessel, a vacuum established in the latter, and the compression cock opened, the greater part of the carbonic acid escapes from the water immediately with considerable violence. As soon as the first portions of the escaped gas have been forced over into the collecting tube the flask is heated on a water bath, gently at first, but afterwards more strongly, until no more gas is evolved from the water. The collecting tube is then removed and a solution of tartaric acid, which has previously been freed from air by exposure in the vacuum apparatus, is drawn into the large glass vessel through the delivery tube which connects this vessel with the collecting tube and pneumatic trough. By opening the compression cock of the water flask the tartaric acid is then admitted to the water, and the last portions of the carbonic acid are thereby expelled. (Lothar Meyer, *Zeitsch. analyt. Chem.*, 1863, 2, 237).

C. Method of E. Dietrich. Applicable to the determination of carbonic acid in cements, bone-black, precipitates and minerals.

The apparatus required consists of a small, wide-mouthed glass bottle, in which to generate the carbonic acid, and two narrow glass tubes, by means of which to measure the gas. The two tubes are of the same length and caliber, and are held in a vertical position upon a table by means of appropriate rods and clamps. Each of the tubes is capable of holding a little more than 100 c. c. The tube nearest the decomposing bottle (called the measuring tube) is graduated to fifths of cubic centimetres, but the other tube has no graduations,—it is a mere pressure tube. Both tubes are cemented at the bottom into iron caps, provided with short, projecting, vertical pipes, to which caoutchouc tubing may be tied. The top of the graduated tube is in like manner cemented with shellac into an iron cap which has a lateral as well as a vertical projection for the attachment of caoutchouc tubes. But the top of the pressure tube is left open, or only partially closed with a perforated cork. The measuring tube is fastened to its supports in a fixed and immovable position, but the pressure tube is so arranged that it may be readily pushed up or down in a vertical plane.

The two glass tubes are connected at the bottom by means of a caoutchouc tube which must be as long as either of the glass tubes. To free the vulcanized rubber from sulphur, boil it for some time in moderately dilute potash lye. A perforated caoutchouc stopper, carrying a straight glass tube, is fitted to the decomposing bottle, and the bottle is put into connection with the measuring tube by means

of a caoutchouc tube, one end of which is tied to the pipe in the stopper of the bottle, and the other end to the lateral projection in the iron cap of the measuring tube. A short piece of caoutchouc tubing, carrying a screw compressor, is attached to the vertical pipe at the top of the measuring tube, so that the tube may be opened or closed at will by turning the screw.

Enough quicksilver is poured into the vertical tubes to fill one of them completely, together with the caoutchouc pipe which connects the two tubes. To prove the tightness of the apparatus, place the stopper in the decomposing bottle, open the screw compressor at the top of the measuring tube, push up the pressure tube until the mercury has risen to the top or 0° mark of the graduated scale, and clamp the pressure tube in that position. Then close the screw compressor on the graduated tube and lower the pressure tube as far as possible. The column of mercury in the measuring tube will instantly fall a little when the pressure is thus removed from it, but if the apparatus be tight the level of the mercury will afterwards remain unchanged as long as the temperature and the pressure of the air remain constant.

In an actual analysis, place a weighed quantity of the carbonate to be examined in the decomposing bottle, together with a small glass tube or bottle two-thirds filled with dilute chlorhydric acid. Cork the bottle tightly, fill the measuring tube with mercury to the zero mark, close the screw compressor, lower the pressure tube and tip the decomposing bottle so that the acid in the tube within it may flow upon the carbonate. When the evolution of gas has ceased, and all parts of the apparatus have again acquired a common temperature, lift the pressure tube until the mercury stands at the same level in it and in the measuring tube, and note the volume of gas in the latter. Correct the observed volume for temperature, barometric pressure, and the tension of aqueous vapor, and calculate the weight of the corrected volume from the known sp. grs. of carbonic acid and air. For Dietrich's table, giving the weights of cubic centimetres of CO_2 under barometric pressures ranging from 720 to 770 m. m., at temperatures from 10° to 25°, see *Zeitsch. analyt. Chem.*, 1865, 4. 142.

The chief source of error to be taken into account depends upon the fact that a considerable quantity of carbonic acid remains dissolved in the liquid in the decomposing bottle. The quantity of carbonic acid thus dissolved is found to be greater in proportion as the quantity of gas evolved is greater. Thus in a case where 92.8 c. c. of carbonic acid gas were developed, 4.6 c. c. of carbonic acid remained dissolved in the liquid in the decomposing bottle, while in another case where 0.9 c. c. of gas were set free only 0.3 c. c. remained dissolved in the same quantity of liquid. Dietrich (see *Zeitsch. analyt. Chem.*, 1864, 3, 166 and 1865,

4. 145) has drawn up tables of corrections to be applied in compensation for this source of error. — As soon as the evolution of carbonic acid ceases, the decomposing bottle should be placed in water of the same temperature as that of the air of the apartment, in order to remove the heat developed by the chemical action. Or, better, the decomposing bottle may be kept in water during the course of the experiment, and, if need be, the gas may be made to flow through a leaden worm sunk in water with the decomposing bottle. — In case more than 100 c. c. of carbonic acid are to be given off from the sample of carbonate under examination, the gas must be measured by portions. To this end, pour the chlorhydric acid, little by little, upon the carbonate, in such manner that the evolution of gas may cease before the measuring tube is completely filled with it. Then slip a screw compressor over the rubber tube which connects the decomposing bottle with the measuring tube, close the tube tightly, and measure the gas which has been evolved; discharge the measured gas, refill the measuring tube with mercury, loosen the compressor attached to the tube of the decomposing flask, and pour another portion of chlorhydric acid upon the carbonate which still remains undecomposed. When a large quantity of carbonic acid is developed in this way, the error depending upon the absorption of gas by the liquid in the decomposing bottle may be readily allowed for. It will be sufficient to measure the chlorhydric acid used, to estimate how much carbonic acid would be absorbed by a similar volume of water at the temperature in question, and add this volume to the measured volume of the evolved gas. Up to 300 or 400 c. c. the errors incidental to measuring do not materially affect the accuracy of the results. (E. Dietrich, *Zeitsch. analyt. Chem.*, 1864, 3. 162 and figure).

D. *Method of Rumpf.* Seeking to simplify the method of Dietrich, Rumpf (*Zeitsch. analyt. Chem.*, 1867, 6. 398) has constructed an apparatus which may readily be made from materials to be found in every laboratory. This apparatus consists simply of an ordinary Mohr's burette of from 30 to 50 c. c. capacity, a hydrometer jar, test tube, and small, wide-mouthed bottle, together with a cork and connectors of glass and rubber tubing. The carbonate to be analyzed is decomposed in the bottle and the evolved gas measured in the burette which is inverted for the purpose in mercury contained in the hydrometer jar.

To construct the apparatus, fit a caoutchouc stopper, having three holes, to the decomposing bottle; fix a thermometer in the middle hole of the stopper, and a short straight glass tube in each of the other holes. To one of the projecting glass tubes tie a short rubber connector, and close it with a spring clip or screw compressor. To the other projecting tube tie one

end of a thick rubber tube, the other end of which has been previously tied to the point of the burette. — Put a weighed quantity of the carbonate to be analyzed into the decomposing bottle together with a short test tube two-thirds filled with a measured quantity of chlorhydric acid. Replace the stopper, open the spring clip, and sink the burette in the mercury in the hydrometer jar until the last division mark upon the burette is level with the surface of the mercury. Close the spring clip and tip the bottle so that acid may flow out of the test tube upon the carbonate. When the evolution of gas has ceased, take hold of the rubber covered point of the burette, and push the latter into the mercury until the surface of the metal is at the same level inside and without the tube. Read off the number of c. c. of gas in the burette; take the height of the thermometer and barometer and proceed to calculate the weight of the gas, taking care to allow for the tension of the aqueous vapor contained in the gas, and for the volume of gas which remains dissolved in the liquid in the decomposing bottle. (Compare the description of Dietrich's method, above).

E. Method of Scheibler. Employed extensively in Germany by sugar manufacturers, for estimating the proportion of carbonate of calcium in bone-black. The process is applicable to the analysis of any carbonate which can be decomposed by cold chlorhydric acid, is easy of execution and yields very accurate results. The rather elaborate apparatus required may be obtained of the dealers in German chemical wares. For a figure and detailed description of it see *Fresenius's Quantitative Analysis*, London, 1865, p. 712, or either of the later editions. The method here alluded to must not be confounded with another process devised by Scheibler for estimating carbonic acid in a mixture of gases by absorption in potash lye. (See Hydrate of Potassium).

F. Method of Russell. Applicable to the determination of carbonic acid in carbonates, and to the valuation of oxides, such as binoxide of manganese, which give off carbonic acid when mixed with oxalic and sulphuric acids. — The apparatus required differs but little from that devised by Williamson & Russell for the analysis of gases (see *Proceedings of London Royal Soc.*, 9, 218; further, *Journ. London Chem. Soc.*, 1868, 21, 128). The latter consists simply of a tubular pneumatic trough, a eudiometer tube and a pressure tube with clamp-rods to hold the tubes in place.

According to Russell, the pneumatic trough may be made of sheet gutta percha half an inch thick. Seen from above this trough is a pear-shaped box, $6\frac{1}{2}$ inches long, in the clear, by $3\frac{1}{2}$ inches wide at the broadest part. The sides of the trough are 3.5 inches high, and at

its centre there is a well in which the eudiometer and pressure tube may be sunk at will. The broader part of the trough is made circular so that there may be placed in it a tall glass sleeve large enough to envelope both the eudiometer and the pressure tube. During an experiment this outer sleeve is kept full of water, in order that the contents of the eudiometer may be maintained at a constant temperature. The opening of the well is 2.5 inches long by $1\frac{1}{8}$ inches broad. One part of the well, devoted to the pressure tube, is 14 inches deep, measured from the bottom of the trough, while the part reserved for the eudiometer has a depth of 19 inches. The narrower part of the trough, not occupied by the water-sleeve has a depression or channel in the middle. This channel is $\frac{5}{8}$ of an inch wide and its depth gradually increases from the edge of the trough to 1.75 inch at the side of the well. (See figure in *Journ. London Chem. Soc.*, 1868, 21, 129). The eudiometer is similar to that of Bunsen (see his *Gasometry*), viz., a straight glass tube closed at the top, some 500 or 600 millim. long by 20 millim. in diameter. It is provided with platinum wires at the top and graduated and calibrated according to Bunsen's plan. The "pressure tube" is simply a straight glass tube of about the same diameter as the eudiometer and closed at the top. Its purpose is to hold a constant quantity of air to be used as a standard of comparison in measuring any gas in the eudiometer. To prepare the pressure tube for use, a very small drop of water is placed at the closed end, and mercury then poured into the tube until most of the air has been displaced. The tube is then inverted in the mercury trough and the height of the mercury in the tube marked off once for all. After this has been done, any effect which the rise or fall of either barometer or thermometer would produce on the bulk of the air in the tube may be exactly counteracted by raising or lowering the tube in the mercury-trough until the mercury again comes to the mark. Before filling the eudiometer with mercury a drop of water is placed in it so that the gas to be measured may always be saturated with aqueous vapor. Any alteration of temperature in the water of the sleeve that surrounds the tubes which may occur during an analysis will not affect the accuracy of the measurements, provided both tubes have undergone the same change of temperature. To ensure an even temperature, the water in the sleeve is agitated from time to time with a wooden stirrer. Before proceeding to measure a gas in the eudiometer the gas is brought to exactly the same tension as that of the standard volume of air in the pressure tube. To do this the two tubes are placed side by side and the eudiometer is raised or lowered until the column of mercury within it is of the same height as that which is required to bring the air in the pressure tube to the original volume. For details relating to

the management of the apparatus, see Williamson & Russell's paper in *Journ. London Chem. Soc.*, [2.] 2. 238.

For estimating carbonic acid or any other gas by measurement, the eudiometer above described is replaced by a somewhat larger graduated tube. This "measuring tube" may be 29 inches long and rather more than 0.75 inch in internal diameter. At the top it is drawn out to a comparatively narrow tube, which is bent at a right angle and left open. The bent part is about half an inch long. A piece of caoutchouc tubing 3.5 inches long is pushed over the projecting bent tube as far as it will go, then bound tightly to the glass and cemented all around with marine glue. The glue is applied as hot as possible so that it may adhere firmly to the glass and make a perfect joint. The rubber tubing should be very thick, the outside diameter being as much as half an inch, while the bore of the tube is only $\frac{1}{8}$ or $\frac{1}{4}$ of an inch. The inside of the tube should be well vulcanized, but the rest of the tube only slightly so.

The carbonate of calcium and acid, or other materials from which the gas is to be generated, may be placed in a small generating flask made by blowing a bulb at the end of a glass tube. The diameter of the glass tube should be such that the rubber tube above described will just fit into it. The rubber tube thus forms a sort of stopper to the flask and connects it in the simplest way with the measuring tube. The manipulations are very simple. A drop of water is placed in the measuring tube and the latter, with the flexible tube attached to it, is put in its position within the water sleeve and clamped, just as a eudiometer would be. To fill the tube with mercury, attach a piece of strong glass tubing, about 2 feet long and slightly tapering at one end, to the flexible tube and sink the measuring tube as far as it will go into the well of the trough. It is not necessary that the well be deep enough to receive the whole of the tube, for by attaching temporarily a thick rubber tube to the end of the glass tube which reaches above the top of the sleeve and applying the mouth to the rubber tube, it is easy to suck up the mercury to a height of several inches. When the mercury has thus been drawn up to within 2 or 3 inches of the top of the mercury tube, pinch the rubber tube for a moment with thumb and finger, and plug it at the end with a bit of glass rod. Elevate the measuring tube so that the flexible tube attached to it shall project above the top of the sleeve, and close this flexible tube with a screw compressor. Withdraw the thick glass tube from the flexible tube, insert the end of the latter into the neck of the generating flask, and loosen the screw compressor so that the flask and the measuring tube may communicate freely one with the other. Bend the flexible tube so that the flask shall be immersed in the water of the sleeve, and fasten the flask in

this position by means of a rubber ring slipped over the clamp-rod which holds the measuring tube in place. As soon as the flask and its contents have acquired the temperature of the surrounding water, proceed to measure the volume of air in the flask and tube, as follows:—Lower the measuring tube into the well until the column of mercury in the tube is of the same height as that in the pressure tube, and note the volume of gas in the measuring tube. This reading gives the amount of air in the apparatus before any of the gas to be estimated has been evolved. Again elevate the measuring tube so that the flask may be brought outside the sleeve, and tip the flask so that the ingredients within it may be mixed and made to react upon one another. The flask may be heated at this stage if need be. A second measurement after the reaction in the flask is completed gives the volume of gas produced. To prevent the substances in the flask from coming in contact out of season, one of them is placed in a small tube, which is lowered into the flask in the usual way, and care is taken not to tip the flask prematurely.

Precautions. To avoid leakage the rubber tube which connects the flask with the measuring tube must be slightly wetted. So long as this joint is kept wet it remains perfectly tight, but if it become dry and there is a high column of mercury in the tube it will probably leak. In order to ensure the presence of moisture, a piece of wick yarn is wound round the joining of the flask and rubber tube and the ends of the yarn allowed to dip into the water of the sleeve. It has been proved, by direct experiment, that the varying amount of bending which rubber tubing of the prescribed thickness will undergo when the flask is sunk in the sleeve does not appreciably alter the volume of air in the measuring tube.

It is important that the caoutchouc tube be as short as possible lest, in determining carbonic acid, a considerable error arise from the absorption of a gas by the caoutchouc. In one experiment in which the carbonic acid from 0.124 grm. of marble was collected in a glass tube, to the top of which was attached a piece of the thick rubber tubing some 8 or 9 inches long, it was found that although there was some air in the tube, as well as the carbonic acid which occupied 201.71 divisions, the gas at the end of one hour had diminished 7.7 divisions, at the end of 2 hours, 9.9 divisions, 3 hours, 11.5 divs., 4 hours, 13.3 divs., and by the next day, 30.3 divisions. With a short piece of the rubber tubing, such as that above described, the amount of gas which disappears is about 0.1 of a division of the tube every five minutes. — In an ordinary gas analysis it is sufficient if we know the relative volumes of gas at the different stages of the analysis; but for the present purpose the necessary data for converting these relative volumes into absolute volumes, and for ascertain-

ing their weight, must be determined. The measuring tube is calibrated in the usual way, and a table of volumes drawn up similar to one for an ordinary eudiometer. The volume of mercury which has been used in the calibration is weighed and the temperature noted. The value of one volume in the table, expressed in cubic centimetres, is then determined by the formula:—

$$C = \frac{w \times (1 + 0.0001815 t)}{13.596 V}$$

in which w is the weight and t the temperature of the constant quantity of mercury which occupies the volume V , used as the standard in the calibration. 0.0001815 is taken as the coefficient of expansion of mercury, and 13.596 as the specific gravity of that metal at 0°C . It is necessary, moreover, to know the temperature and pressure at which the measurement has been made, in order to find the weight of the gas. When the measurements are made by means of a pressure tube, it is only necessary to ascertain once for all what is the temperature and pressure, at the same moment, of the air in the upper part of the pressure tube; the mercury standing exactly at the mark which indicates the constant volume. When the weight of dry gas occupying one tabular volume of the measuring tube has once been calculated from these data, it is only necessary to multiply any volume of that gas, which may be measured in the tube, by this constant, in order to obtain the weight of the gas.

It has been found in practice that the error which might arise from the retention of carbonic acid, dissolved in the liquid of the flask, may be avoided almost entirely by employing only a slight excess of the dilute acid. The process is liable to another source of error, inasmuch as the tension of the gas in the measuring tube may be slightly altered when a little of the acid is carried over into the tube. But it is found, when operating with a flask of about 120 c. c. capacity, that the alteration of tension is very slight unless the reaction in the flask has been unusually violent. It is well, for that matter, to place a loose plug of cotton-wool in the neck of the flask.

The process yields accurate results, is rapidly executed, and requires only small quantities of material. (Russell, *Journ. London Chem. Soc.*, 1868, 21. 310).

3. *By noting the weight of the residue, or by analyzing the residue.* Dissolve the carbonate in a slight excess of chlorhydric acid, or other suitable acid, evaporate the solution to dryness, weigh the residue, and calculate the weight of carbonic acid which is equivalent to it. The method is applicable only to the analysis of carbonates free from impurities, and capable of forming fixed and definite chlorides, or other salts. Instead of weighing the dry chloride, the amount of chlorine contained in it may be

determined as Chloride of Silver, by titration, and from the weight of chlorine found, the equivalent quantity of metal in the residue, and of carbonic acid in the substance analyzed, may be calculated. According to Mohr (*Titrimethode*, 1855, 2. 58) the last named process may be usefully applied in analyzing alkaline carbonates which contain chlorides, and mixtures of carbonates of sodium and chloride of sodium in mineral waters. The chlorine proper to the solution is first determined by titration with nitrate of silver, the mixture is then supersaturated with chlorhydric acid, evaporated to dryness, and again titrated to estimate the chlorine which has taken the place of the carbonic acid.

4. *By absorbing the gas in an alkali.* [Compare Principle I]. This method is convenient of execution, and yields exceedingly accurate results. It is, perhaps, better suited than either of the others for the ordinary requirements of the laboratory. The process may be conducted as follows:—Place a flask of about 300 c. c. capacity, on a piece of wire gauze laid upon a tripod or ring-stand above a lamp, and fit to the flask a caoutchouc stopper provided with two perforations. To one of the holes in the stopper fit a glass tube something more than twice as long as the flask is high; bend the tube twice, near the middle, into the form of an S, in such manner that the bent portion may be wholly outside the cork, while enough of the tube is left straight, at either end, to reach almost to the bottom of the flask; blow a small bulb upon the tube at the middle of the bent portion, *i. e.*, at the centre of the S. To the other hole in the stopper fit a short glass tube, bent at a right angle, to serve as a gas-delivery tube. It is well to blow a bulb on the upright part of the delivery tube, outside the cork, and to grind off the lower extremity obliquely so that drops of water may fall from it. Bring the outer end of the delivery tube into line with a series of absorption tubes arranged as follows:—1st, a bulbous U-tube full of chloride of calcium; 2d, a very small U-tube filled with fragments of glass moistened with 8 or 10 drops of concentrated sulphuric acid and loosely plugged with asbestos at either end; 3d, a U-tube charged with soda-lime and a little chloride of calcium in the ordinary way, and 4th, a U-tube, the inner limb of which is charged with chloride of calcium, and the outer limb with soda-lime or hydrate of potassium. The purpose of this last tube is merely to protect the 3d tube from the moisture and carbonic acid of the air; to the outer end of it attach a piece of rubber tubing 5 or 6 inches long. The 1st tube, which should be comparatively large, is a mere drying tube and is never weighed. The 2d and 3d tubes serve to absorb the carbonic acid, and are weighed together. The purpose of the sulphuric acid in the second tube is merely to show

the rate of flow of the carbonic acid, but since sulphuric acid absorbs a certain amount of carbonic acid, this tube has to be weighed with the others.

After the tubes 2 and 3 have been weighed and tightly connected with the other tubes, place a weighed quantity of the substance to be analyzed in the flask, moisten it with water, cork the flask, and connect its delivery tube with the 1st tube of the series above described. By means of a caoutchouc connector attach a small funnel to the top of the S-tube in the flask, and pour through it a small quantity of mercury to fill the lowermost part of the bend, beneath the bulb, in the S-tube. Then fill the funnel and tube with a mixture of equal volumes of strong nitric acid and water, and suck gently through the caoutchouc tube at the end of the series of absorption tubes, until a little of the acid is drawn past the mercury into the flask. The bulb in the S-tube prevents the mercury from passing over into the flask with the acid.

The carbonic acid set free by the nitric acid is dried by the chloride of calcium in the 1st U-tube, and its rate of flow is made manifest by the bubbles which pass through the sulphuric acid at the bottom of the second U-tube. As soon as the evolution of gas slackens, suck over new portions of the nitric acid into the flask until the carbonate has been completely decomposed. If need be, the flask may be heated gently throughout the process. When no more gas is evolved wash out the S-tube by filling it two or three times with hot water and sucking the water into the flask. Remove the funnel from the top of the S-tube and replace it with a tube filled with soda-lime or hydrate of potassium; then heat the contents of the flask to gentle boiling until the projecting portion of the 1st chloride of calcium tube becomes hot on the side nearest the flask. Extinguish the lamp and, by means of an aspirator fastened to the end of the 4th tube, draw as much air through the apparatus as will amount to at least six times the volume of the flask. After the apparatus has become cold, weigh the 2d and 3d U-tubes. The difference between this second weight of the tubes and the weight before the operation, gives the amount of carbonic acid in the substance analyzed. — The other constituents of the substance may be determined in the nitric acid solution which is left in the flask. By using a definite quantity of standard acid and titrating the excess with a standard alkali, as explained above, in paragraph 1, after the carbonic acid has been expelled, it is easy, in many cases, to determine the quantity of the base with which the carbonic acid was combined. In cases where chlorhydric acid is to be preferred to nitric acid for dissolving the substance, fill one limb of the 1st chloride of calcium tube,—that which is farthest from the flask,—with fragments of pumice stone satu-

rated with anhydrous Sulphate of Copper, and proceed as before.

The 2d tube, charged with sulphuric acid, may be used over and over again for many analyses. So, too, the soda-lime tube may be used repeatedly, subject to the usual rules which apply to this substance. When large quantities of carbonic acid are to be absorbed the soda-lime tube may be replaced by Geissler's potash bulbs, or even by Liebig's bulbs, if the evolution of gas be carefully regulated. (Kolbe, *Annal. Chem. und Pharm.*, 119. 130, and Fresenius, *Quantitative Analysis*, p. 300).

5. *By absorbing the gas with an alkaline earth.* The carbonic acid generated in the apparatus described above, paragraph 4, might, of course, be collected in the form of Carbonate of Barium or Carbonate of Calcium. As a general rule, however, the absorption by soda-lime is greatly to be preferred.

Principle III. Power of changing the color of blue litmus to violet.

Application. Rough estimation of the free carbonic acid in mineral waters.

Method. Prepare a standard solution of dilute sulphuric acid (see Acidimetry) of such strength that 1 c. c. of it shall contain 10 milligrammes of SO_3 ; also a solution of litmus, by digesting a quantity of the solid in an equal weight of cold water. There is required also, a concentrated solution of caustic soda containing some carbonic acid, such as may be found upon the shelves of any laboratory.

Measure out about 450 c. c. of distilled water, add to it 1.5 c. c. of the litmus solution and 5 c. c. of the caustic soda. Dilute the mixture with water to the volume of 500 c. c., take out with a pipette 3 several portions of 100 c. c. each, of the liquid, and pour them into three beakers. Place the beakers on a white ground in strong daylight, and pour the standard acid from a burette into each beaker in succession, until its contents appear distinctly violet colored. Towards the close of each operation it is necessary to wait one or two minutes after each addition of acid, in order that the change of color, when it does occur, may become distinctly visible. The experiment in the 1st beaker will give an approximately correct result, so that in the second and third trials the operator will be able to hit the point of coloration with tolerable accuracy. Select the most accurate of the three experiments, to the exclusion of the other two, multiply by 5 the number of c. c. of acid consumed in that case, and record the product of this multiplication as the quantity of acid corresponding to 5 c. c. of the soda solution.

It is to be observed that the color of blue litmus is not changed to violet by bicarbonate of sodium, but only by free carbonic acid; hence, when dilute sulphuric acid is cautiously added to a solution containing carbonate of

sodium, no violet coloration will appear until the sodium compound has all been converted into sulphate and bicarbonate, and some carbonic acid has actually been set free from the latter by the addition of a drop of sulphuric acid in excess. It will be noticed, also, that since all the carbonic acid is in the state of a bicarbonate at the close of the neutralization, two molecules of this acid must be reckoned as equivalent to, or as replacing, one molecule of SO_3 . Hence, if 1 c. c. of the standard sulphuric acid contains 10 milligrams. of SO_3 , the c. c. will correspond to 11 milligrams. of CO_2 .

To perform an analysis, add 5 c. c. of the soda solution, or 10 c. c. if need be, to 450 or 500 c. c. of the mineral water under examination, and mix the two liquids. Without heeding any turbidity which may appear in the liquor, measure out as before three separate portions of 100 c. c. each, add to each portion 4 drops of the litmus solution, and pour in the standard sulphuric acid until the liquid exhibits a violet tint. More care and attention should be given to the experiment upon the second portion of liquor than to the first, and still more to the third than to the second. Choose the best of the three experiments, as before; subtract the number of c. c. of acid required to produce the violet coloration in the mixture of mineral water and soda, from the amount of acid which was required to produce the coloration with the soda alone, and multiply the difference by 0.011 (the value of the standard acid in terms of CO_2) in order to obtain the weight of the carbonic acid in grammes.

In most cases the quantity of mineral water taken had better be measured after the admixture of the soda, in order to avoid losing much carbonic acid. If the sample of water to be examined is contained in a bottle, cool it to about 4° , remove the stopper quickly, pour out a little of the water, and add the soda to the rest. — The process is of value for some purposes, but requires a practised eye. (Kersting, *Annal. Chem. und Pharm.*, 94. 112).

Principle IV. Power of absorbing the heat which radiates from ignited carbonic acid gas.

Tyndall has observed that though carbonic acid gas is one of the weakest absorbents of the heat which radiates from a glowing solid, it has, on the contrary, a remarkable power of absorbing the heat radiated from a flame of burning carbonic oxide. — The fact not only furnishes a delicate qualitative test of the presence of carbonic acid in a mixture of gases, but has been successfully applied to the estimation of carbonic acid in air expired from the lungs. It is not improbable that the process may be found more accurate and convenient than any other for determining the proportion of carbonic acid in air, in cases where

a large number of experiments are to be made. (*Zeitsch. analyt. Chem.*, 1868, 7. 151. For a description of the apparatus employed, see Tyndall's *Heat a Mode of Motion*).

Carbonate of Ammonium.

Principle I. Power of neutralizing acids.

Application. Estimation of carbonate of ammonium in commercial samples.

Method. See Alkalimetry. Mohr (*Titrir-methode*, 1855, I. 63) found that the results obtained by supersaturating carbonate of ammonium with oxalic acid and titrating the excess of the latter with caustic soda, were liable to wider variations than those of most other alkalimetric processes. After the expulsion of the carbonic acid the hot acid liquor must be cooled completely before adding any of the standard caustic soda, lest some ammonia be set free by the latter.

Principle II. Volatility.

Application. Estimation of carbonates in natural waters.

Method. Add to 200 c. c. of the filtered water about 0.5 grm. of chloride of ammonium, distill off half the solution and receive the distillate in 10 c. c. of very dilute standard sulphuric acid. Boil the mixture of distillate and acid to expel carbonic acid gas, then allow it to cool, and determine how much of the standard acid still remains free, by titrating with weak standard soda (see Alkalimetry, and above). The process is said to yield good results. (Chevalet, *Bull. Chem. Soc. Paris*, 1868, p. 90).

Carbonate of ammonium is often used as a precipitant, solvent and decomposer of sundry metallic carbonates. It is used also to convert bisulphates of the alkalies to neutral salts. To be fit for use as a reagent it should leave no residue when heated in a platinum dish.

Carbonate of Ammonium and of Magnesium.

See Carbonate of Magnesium and of Ammonium.

Carbonate of Barium.

Principle I. Fixity when not too strongly heated.

Application. Estimation of barium in salts with organic acids.

Method. Heat the salt carefully in a covered platinum crucible until no more fumes are evolved. Then take off the lid, lay it flat upon one side of the triangle which supports the crucible, and lay the crucible flat, or obliquely upon its side with the open end resting on one edge of the cover. Ignite the crucible in this position until the carbon is all consumed and the residue has become perfectly white. Since a portion of the carbonate of barium is apt to be reduced to the condition of oxide by the ignition in contact with carbon, the cold residue must be moistened with a concentrated solution of carbonate of ammonium, in order to reconvert the oxide into carbonate. After adding the carbonate of ammonium evaporate the

mixture to dryness on a water bath, heat the dry residuc moderately, cool, and weigh. Compare Carbonate of Calcium. — A certain quantity of the substance is almost always lost during the ignition, from fine particles of matter being carried away mechanically by the gaseous products of the distillation. This source of error, however, is the less considerable in proportion as the crucible is heated more slowly. With proper care the process yields satisfactory results.

Properties. Carbonate of barium is unalterable in the air, even when heated to redness. In the intense heat of a forge, however, or blast furnace, it slowly gives up the whole of its carbonic acid (Abich, *Poggendorff's Annalen*, 1831, 23, pp. 308, 314). The presence of aqueous vapor favors the escape of the carbonic acid. The composition of the salt is as follows:—

Ba	:	:	:	137	:	:	:	77.69
CO ₂	:	:	:	60	:	:	:	22.51
				197				100.00

Principle II. Sparring solubility in water.

Applications. The process may be employed for estimating barium in all barium salts which are soluble in water, but is rarely used for this purpose excepting in those cases where the estimation of the metal as Sulphate of Barium would be inadmissible. It is employed also for separating Ba from K, Na, Mg, Mn, etc., and for estimating carbonic acid.

Methods.

Estimation of Barium in solutions of its salts. Mix the moderately dilute solution with ammonia-water in slight excess, add the carbonate of ammonium as long as a precipitate falls, and leave the mixture at rest for 12 hours in a warm place. Collect the precipitate upon a filter, wash it with water, to which a little ammonia has been added, then dry, ignite, and weigh. See Principle I. — Since carbonate of barium is not absolutely insoluble in ordinary water, and is soluble to no inconsiderable extent in aqueous solutions of ammonium salts, the results obtained by this method are usually a little lower than the truth. Care must always be taken to keep the proportion of chloride, nitrate or other salt of ammonium in the solution as small as possible.

It is to be observed that carbonate of barium cannot be precipitated from solutions which contain a citrate or metaphosphate of either of the alkali metals.

Separation of Ba from K, Na and Mg. The process is employed in certain cases for separating barium from potassium, sodium and magnesium, though it is, on the whole, less accurate and convenient than the method described under Sulphate of Barium. It is employed, for example, when barium is to be separated from a mixture of both potassium and sodium, since the mixture of alkalies in the filtrate from carbonate of barium can easily be converted into chlorides, and analyzed as such.

But if only one of the alkalies were present, the barium would always be thrown down as Sulphate of Barium, and the alkali weighed as a sulphate. — The process finds application, also, in cases where a mixture of Ba, Sr and Ca is to be separated from K and Na, or from K, Na and Mg. The precipitation of the carbonates of the three metals of the alkaline earths is effected in precisely the same way as if only barium were present. Chloride of Ammonium is added to keep up magnesium in case any of that metal is contained in the substance to be analyzed. But since this chloride of ammonium prevents the precipitation of some barium and calcium, the filtrate from the precipitated carbonates must be subjected to further treatment as follows:—Add to the filtrate a small quantity of dilute sulphuric acid, no more than 3 or 4 drops, together with a few drops of a solution of oxalate of ammonium and let the mixture stand 12 hours in a warm place. A mixed precipitate of sulphate of barium (and strontium) and oxalate of calcium will fall. Collect this precipitate on a small filter and treat it with dilute chlorhydric acid. The oxalate of calcium will dissolve, together with a little oxalate of magnesium which is sometimes thrown down with it, while the sulphate of barium (and strontium) is left as an insoluble residue upon the paper. To recover the magnesium just mentioned, saturate the chlorhydric acid filtrate with ammonia-water, allow the re-precipitated oxalate of calcium to settle, filter, and add the filtrate to the mixture of magnesium and alkalies. Sometimes a little insoluble carbonate of magnesium goes down with the carbonate of barium, etc.; it may be recovered during the process of separating these elements.

To separate Potassium from a mixture of Ba, Ca and Mg, in a solution free from ammonium salts, heat the liquid to strong boiling and add to it a solution of carbonate of sodium, drop by drop, as long as any precipitate falls. Continue to boil until the voluminous precipitate has become compact and granular. It is easy to wash out all the potassium from the precipitate if the boiling has been continued long enough. But the method will be found, in most cases, to be inferior to that of precipitating the potassium directly as Chloroplatinate of Potassium. (Stohmann, *Zeitsch. analyt. Chem.*, 1866, 5, 307).

Separation of Ba from Mn. See Carbonate of Manganese.

Indirect separation of Ba from Ca and Sr. See Carbonic Acid (Volatility of, — methods by simple ignition, and by ignition with an acid salt).

Estimation of Carbonic Acid.

1. Absorption in baryta-water.

Many chemists have estimated carbonic acid by absorbing the gas in baryta-water and weighing the precipitated carbonate, in the manner above described. De Saussure in partieu-

lar, sought to perfect the process by washing the carbonate of barium with a saturated solution of this substance, in place of water, and did unquestionably obtain accurate and valuable results in that way,—as Boussingault and others have done after him. — The modern methods are as follows:—

A. *Method of Mohr & v. Gilm (Wien. Akad. Bericht, 24. 279)*, employed for estimating the proportion of carbonic acid in atmospheric air. By means of an aspirator of at least 30 litres capacity, some 60 litres of the air to be analyzed are slowly drawn through an absorption tube containing a solution of hydrate of barium; the precipitate of carbonate of barium which forms is collected upon a filter out of contact with the air, the tube and precipitate are washed first with distilled water saturated with carbonate of barium, and afterwards with pure water which has been recently boiled. The carbonate of barium upon the filter and in the tube is then dissolved in dilute chlorhydric acid, the solution evaporated to dryness, the residue ignited gently and the amount of chlorine contained in it determined as Chloride of Silver. Or the amount of barium may be determined as Sulphate of Barium. Every atom of Ba, or every two atoms of C^l will represent a molecule of CO₂.

To prepare the absorbent liquid, dissolve crystallized hydrate of barium in a warm dilute solution of caustic potash, and filter the mixture. Since some carbonate of barium is always precipitated on the addition of the potash lye, the clear solution obtained necessarily contains all the carbonate of barium it is capable of dissolving. — For the absorption tube, choose a tube a metre long, and about 15 m. m. wide. Draw out the upper end of the tube, and at some distance from its lower end bend the tube at an angle of 140°–150°. Fix the tube in such a position that its longer limb shall incline at an angle of 8° or 10° to the horizontal and fill the tube half full of the clear baryta-water. By means of a perforated cork, fit a narrow glass tube into the wider end of the absorption tube, for the admission of air, and connect the other end of the absorption tube with the aspirator. It is well to interpose a couple of little flasks, charged with the baryta-water, between the absorption tube and the aspirator, in order to be sure that the whole of the carbonic acid has been absorbed from the air.

Since, in passing through the absorption tube, the air is compelled to force its way against a column of liquid, it is essential that the aspirator employed should be provided with a small manometer, in order that the volume of air may be accurately measured. The height of the column of mercury in the manometer must be deducted from that observed in the barometer at the time of the experiment.

For filtering the carbonate of barium, v. Gilm uses a double funnel, arranged as fol-

lows:—By means of a perforated cork, fit to a sufficiently wide-mouthed bottle a large funnel with wide throat. The rim of the funnel should be ground so that it can be covered tightly with a glass plate. Fit a cork to the upper part of the throat of this funnel, perforate the cork and cut a groove in its side. Through the hole in the cork thrust the tube of a second funnel considerably smaller than the first, and place the filter in this inner funnel. During the operation of filtering, the large funnel is kept closed as much as possible with a glass plate. Air can of course pass freely from the bottle into the large funnel through the slit or groove in the inner cork.

According to observations of A. Mueller (*Zeitsch. analyt. Chem.*, 1862, 1. pp. 84, 149), this process is open to the objection that filter paper has the power to absorb considerable quantities of baryta out of baryta-water, and to retain it so forcibly that it cannot be washed out.

The precipitated carbonate of barium might of course be decomposed with an acid in an appropriate apparatus, and the Carbonic Acid weighed or measured as such, instead of being treated as above described, or in addition to this treatment.

B. *Methods of Hadfield, of Pettenkofer, and of A. Mueller.* See below, under Principle III (Power of neutralizing acids).

2. *Absorption in an ammoniated solution of chloride of barium.* This method may be employed in the analysis of mineral waters, air, and other gaseous mixtures. It was formerly sometimes used for estimating carbonic acid set free from carbonates by the action of acids, but is now known to be inferior to the methods described in the preceding paragraphs, and to several of the methods described under Carbonic Acid.

Prepare a quantity of an ammoniated solution of chloride of barium, as follows:—Mix an aqueous solution of chloride of barium with an excess of ammonia-water, boil the mixture for a few minutes and filter the hot liquid quickly, in order to remove the carbonate of barium formed by carbonic acid contained in the ammonia-water. After the mixture has once been boiled, take care to protect the liquid as much as possible from contact with carbonic acid of the air. Pour 50 or 80 c. c. of the clear liquid into a light flask of about 300 c. c. capacity, and close the flask tightly with a caoutchouc stopper. Without removing the stopper, weigh the flask together with the barium solution, and pour into the flask enough of the mineral water, or other solution of carbonic acid to be tested, to nearly fill it, then replace the cork immediately, shake the flask, and again weigh it with its contents. The difference between the first and second weighings will give the weight of the mineral water taken. Instead of weighing the mineral water it may be measured as follows:—Measure out

the 50 or 80 c. c. of ammonio-barium solution to be placed in the flask, by means of a pipette provided with a rubber ball or soda-lime tube, so that no carbonic acid can enter it from the lungs; then pour the mineral water into the flask, cork the flask, and scratch the glass with a diamond, or paste upon it a bit of paper, with shellac, to mark the height of the liquid. After the carbonate of barium has been precipitated and the experiment finished, fill the flask with water up to the mark, measure the water in a graduated cylinder, and subtract from it the quantity of barium solution in order to obtain the true volume of the mineral water. For another method of measuring the mineral water, see Carbonate of Calcium.

Place the flask in a pan of water, loosen its cork, heat the water to boiling, and keep the flask in the boiling water for an hour or two. Then re-cork the flask, allow its contents to settle out of contact with the air, and proceed to collect the carbonate of barium on a filter, in the manner to be described directly.

It is to be observed that although the liquid in the flask usually becomes turbid as soon as the mineral water is introduced, the mixture must, nevertheless, be heated a long time in order that all the carbonic acid may be thrown down, for at temperatures much below boiling carbonate of barium is soluble to no inconsiderable extent in a solution of chloride of ammonium. The contents of the flask must never be heated to actual boiling, however, for in that case some of the carbonic acid would escape in the form of carbonate of ammonium.

Instead of heating the mixture almost to boiling for an hour or two, it may be left during half a day in a place heated to 80° or 90°.

For filtering, provide a funnel with glass cover, quickly decant the clear liquid from the flask into the filter, and cover the funnel. Nearly fill the flask with warm water, replace the cork, shake the contents of the flask, let the precipitate subside in the flask until the filter has become empty, and again decant the tolerably clear liquor from the flask into the filter. Wash once more by decantation, then transfer the precipitate to the filter, and wash with warm water until the washings no longer give any precipitate when tested with nitrate of silver. In case the last portions of the precipitate cannot be rubbed off the flask, dissolve them in a little dilute chlorhydric acid, mix the solution with pure carbonate of sodium, and collect the precipitate which forms, upon a small separate filter. Dry, ignite and weigh the precipitate as in Principle I.

If the substance analyzed contained no other substance besides carbonic acid capable of precipitating barium or of being precipitated by ammonia, the weight of the carbonic acid may be calculated directly from that of the carbonate of barium. But if, on the other hand, the precipitate is contaminated with phosphate of barium, carbonate of calcium, ferric oxide, or

the like, the proportion of Carbonic Acid contained in it must be specially determined.

This method, as well as the analogous method mentioned under Carbonate of Calcium, was formerly often employed, but is now held in comparatively slight esteem. The chief objections to it are found in the solubility of carbonate of barium in water, the difficulty of obtaining an ammoniated barium solution, in the first place, absolutely free from carbonic acid; in the liability of this solution to absorb carbonic acid from the air; in the risk of driving off some carbonic acid in the form of carbonate of ammonium; and in the very decided tendency of carbonate of barium to remain dissolved in a solution of chloride of ammonium. It may readily happen that appreciable quantities of carbonate of barium (or of calcium) may remain dissolved throughout the analysis in case the proportion of chloride of ammonium in the liquid be excessively large or the liquid itself be largely diluted with water. — To guard against the various sources of error, it was customary to operate at one and the same time upon several different portions of the mineral water. — It may here be said that the idea advanced by Kolbe (*Handwörterbuch der Chem.*, 1. Supplem., p. 157) and recently defended by Fresenius (*Zeitsch. analyt. Chem.*, 1863, 2. 49 and 1866, 5. 321) that the retention of carbonate of barium in solution before boiling, is due to the change of carbonic into carbamic acid, is unsupported by any experimental evidence. The erroneous character of the conception has been shown by Carius (*Annal. Chem. und Pharm.*, 1866, 137. 108) and by old observations of my own (*Amer. Journ. Sci.*, 1858, 25. 41; and *Dictionary of Solubilities*).

Instead of drying and weighing the precipitated carbonate of barium, it may be decomposed with an acid and the resulting gas measured (see below), or absorbed in soda-lime and weighed (see below). Or the proportion of carbonic acid may be determined by the Alkalimetric method (see also below, Principle III). But for determining carbonic acid in that way, it had better be precipitated in the form of Carbonate of Calcium.

Properties. Precipitated carbonate of barium is a soft, white powder, soluble in about 48,000 parts of cold water absolutely free from carbonic acid (Bineau), and in 12 or 14,000 of cold water which has been recently boiled to expel most of its carbonic acid. It appears to be but little if any more soluble in hot than in cold water. The aqueous solution has a faint alkaline reaction. The solution in carbonic acid water is also alkaline. — The precipitate is far more readily soluble in neutral solutions of ammonium salts, such as the chloride or nitrate of ammonium, than in water; but is almost completely insoluble in cold water which contains free ammonia and car-

bonate of ammonium; one part of the precipitate requiring in that case more than 140,000 of the liquid for its solution. When boiled with a solution of chloride of ammonium, carbonate of barium is rapidly dissolved with formation of chloride of barium and evolution of carbonate of ammonium. Carbonate of barium dissolves also to a slight extent in aqueous solutions of most of the salts of potassium and sodium. In cold water saturated with carbonic acid, carbonate of barium dissolves in the proportion of 1 part to about 600 parts of the liquid. (Compare Principle I).

The comparatively large molecular weight as well as the more sparing solubility of carbonate of barium are reasons for preferring it to carbonate of calcium, but the precipitate is apt to be more bulky and less easily filtered than that from the calcium salt.

Principle III. Power of neutralizing acids.

Applications. Estimation of barium and of carbonic acid.

Methods.

A. Estimation of barium. Similar to the estimation of calcium described under Carbonate of Calcium.

B. Estimation of carbonic acid.

1. *Method of Pettenkofer (Annalen Chemie und Pharm., 2d Supplement volume, page 23).* In this process a definite volume of the air or mineral water to be analyzed is mixed with a measured quantity of baryta-water of known strength; the carbonate of barium which forms is allowed to settle, and a measured portion of the clear supernatant liquid is finally titrated with standard oxalic acid, in order to determine how much of the hydrate of barium in the liquid has remained uncombined with carbonic acid. The difference between the amount of oxalic acid required to neutralize the uncombined hydrate of barium and that required to saturate the baryta-water originally employed, will be equivalent to the amount of carbonic acid in the sample of air or water taken.

To prepare the standard oxalic acid, dissolve 2.8636 grms. of crystallized oxalic acid in water, and dilute to the volume of a litre. 1 c. c. of the liquid will correspond to 1 milligram. of carbonic acid.

The baryta-water employed must be free from any trace of caustic potash or caustic soda, for it is impossible to titrate baryta-water with oxalic acid in presence of an alkaline oxalate (see Hydrate of Barium).

The baryta-water should be strong or weak accordingly as there is more or less carbonic acid in the air or water to be examined. If the proportion of carbonic acid is comparatively large, it is well to use strong baryta-water prepared by dissolving 21 grms. of crystallized hydrate of barium to the litre, but in case the quantity of carbonic acid to be determined is small, a liquid which contains no more than 7 grms. of the crystallized hydrate

to the litre, is to be preferred. Of the stronger baryta-water 1 c. c. will correspond to about 3 milligrams. of carbonic acid and 1 c. c. of the weaker liquid will be equivalent to about 1 milligram.

To standardize the baryta-water transfer 30 c. c. of it to a small flask and pour in the standard oxalic acid from a burette, little by little, until the liquid is just neutralized. After each addition of the acid, close the flask with the thumb, and shake the liquid. To determine the point of neutralization take up a drop of the liquid upon a glass rod and touch it to a piece of delicate turmeric paper. When a drop of the liquid ceases to produce a browning upon the paper the neutralization is known to be complete. In case too many drops of the oxalic acid happen to be added in this first trial, the experiment may be repeated as follows:—Measure off a second 30 c. c. portion of the baryta-water, add to it at once as much of the standard oxalic acid, to within a c. c. or half a c. c., as was used before; then add the acid drop by drop, and test the liquid on turmeric paper after each drop, until the neutralization is complete. A third experiment should agree with the second to 0.1 c. c.

The details of the actual analysis of a mineral water will be found in the description of the lime-water process under Carbonate of Calcium.

In order to determine the proportion of carbonic acid in air, select a bottle of about 6 litres capacity, having a tightly ground glass stopper, and accurately determine its capacity. Dry the bottle thoroughly and by means of a pair of bellows fill it with the air to be analyzed. Pour into the bottle 45 c. c. of the dilute standard baryta-water, and spread the liquid repeatedly over the inner surface of the glass without shaking the bottle any more than is necessary. In the course of about half an hour the whole of the carbonic acid will be absorbed. Then pour the turbid liquid from the bottle into a glass cylinder, close the latter securely from the air, and leave the liquid at rest until it has become clear. By means of a pipette take up 30 c. c. of the clear liquor, transfer it to a flask, and neutralize with the standard oxalic acid. Since only 30 c. c. out of the original 45 c. c. of baryta-water have been employed, the number of c. c. of oxalic acid required to effect neutralization must be multiplied by 1.5. Deduct the product from the number of c. c. required for 45 c. c. of the standard baryta-water. The difference will show how much of the hydrate of barium has been converted into carbonate, and thereby indicate the amount of the carbonic acid.

Instead of measuring the air in a bottle as above described, it may of course be drawn through tubes charged with a measured quantity of standard baryta-water, by means of an aspirator, as described under Principle II, on p. 95. For Pettenkofer's arrangements for ef-

fecting the absorption, see his original memoir, as cited above.

2. *Method of A. Mueller (Zeitsch. analyt. Chem., 1862, l. 147, and figure).* This method is said to be peculiarly well suited for the determination of carbonic acid in soils, and, in general, for the determination of small quantities of the acid in presence of other volatile substances. It may be employed also for estimating carbonic acid in air, and for experiments on fermentation.

Grind a plate of glass to fit the top of a broad glass cylinder or jar about 100 millim. high and wide. Set a tripod of glass or platinum in the cylinder, and suspend from the tripod a shallow, conical glass vessel of about 40 c. c. capacity. This smaller or "absorption" vessel must be light, and its mouth, though much narrower than the bottom, must be tolerably wide. The top of this vessel also should be ground and fitted with a glass plate. Some forms of ink-stands answer very well for the absorption vessel. There will be needed also a small porcelain crucible of about 15 c. c. capacity.

Prepare standard solutions of nitric acid and of caustic baryta (see Alkalimetry). The baryta solution may be made by mixing a solution of chloride of barium with soda lye. Its strength should be reckoned not in terms of centimetres, but in terms of grammes.

For the analysis weigh out a quantity of the soil, or other substance containing a carbonate, place it in the bottom of the larger glass vessel, and pour upon it 15 or 20 c. c. of water. Place in the porcelain crucible a quantity of some strong non-volatile acid, such as sulphuric, phosphoric, tartaric or lactic acid, more than sufficient to decompose the whole of the carbonate, and set the crucible upon the soil.

Weigh the absorption vessel with its cover, pour into it a quantity of the standard baryta water and again weigh. Remove the glass plate from the absorption vessel, place the latter on the tripod, smear the top of the larger vessel with tallow, close it tightly with its glass plate, and incline the vessel carefully so that some of the acid may flow out of the crucible upon the soil. Repeat the dose of acid from time to time, and then leave the apparatus at rest for a day or two, until the whole of the carbonic acid has been absorbed by the baryta-water. — The rate of evolution of the carbonic acid can be judged of by the appearance of the baryta solution. So long as carbonic acid is generated rapidly, crusts of carbonate of barium will form upon the surface of the liquor as often as the old crust is made to sink by shaking the apparatus. When a crust no longer forms, it is evident that no more carbonic acid is being set free. Wait until the whole of the carbonic acid has been absorbed by the baryta-water, then cover the absorption vessel with its glass plate, and again weigh it with its contents. By means of a syphon and aspirating flask, suck over as much of the clear

liquid as possible into a tared flask which contains a weighed quantity of the standard nitric acid, and again weigh the flask after the addition of the baryta solution. Finally titrate the nitric acid still left free in the flask, in order to estimate the amount of baryta which was added to it. The calculation is as follows:—

If w = the weight of carbonic acid absorbed,
 a = the weight of the baryta before the absorption,
 c = the weight of that portion of the baryta solution taken for titration after the absorption,
 b = the weight of baryta in c ,
 d = the sum of the weights of the baryta solution and the carbonate of barium precipitated in it; and

$$G = \frac{\text{BaO}}{\text{CO}_2} = 3.477, \text{ then}$$

$$w = \frac{a(c-b) - bd}{G(c-b) - b} = \frac{a(c-b) - bd}{3.477(c-b) - b}.$$

It is not practicable to operate with a determined volume, instead of a definite weight of the baryta solution, for the weight of the solution varies constantly during the experiment, both from changes of temperature and from the absorption of more or less aqueous vapor by the acid in the jar. Neither can the baryta solution be filtered after the absorption, for filter paper has the power to absorb considerable quantities of baryta, and to abstract it from the solution. — A correction may be applied for the carbonic acid naturally present in the atmospheric air originally contained in the apparatus, or, better, the apparatus may be filled beforehand with air free from carbonic acid.

In case the soil, or other substance analyzed, evolves chlorhydric acid or other volatile acid on being treated with strong acids, the process is modified to the extent that the amount of baryta in the solution is determined before and after the absorption, by precipitating it in the form of Sulphate of Barium.

3. *Old method of absorption in ammoniated baryta-water.* See above (Principle II) and under Carbonate of Calcium.

Principle IV. Decomposition of by solutions of the salts of iron, aluminum, manganese and chromium; by phosphoric and arsenic acids; and by many other saline solutions and acids; the metals or acids in question being at the same time precipitated in the form of hydrates, or of basic salts.

Applications. Separation of Al from Mg, Ca, Zn, Mn, Ni, Co and Fe (see Hydrate of Aluminum). Separation of Fe from Ba, Sr, Ca, Mg, Zn, Mn, Co, Ni and Fe (see Hydrate of Iron). Separation of Cr from Zn, Mn, Ni, Co and Fe (see Hydrate of Chromium). Separation of P_2O_5 from Fe, Al, Ba, Sr, Ca, and all other oxides not precipitable by carbonate of barium (see Phosphate of Iron). Separation of As from Ba, Ca, Sr; Zn, Mn, Ni and Co (see Arseniate of Iron). — For lists of the compounds precipitable by carbonate of barium, see that substance in Dictionary of Solubilities.

For use as a reagent, carbonate of barium

may be prepared as follows:—Dissolve a quantity of crystallized chloride of barium in hot water, filter the solution and heat it to boiling. Prepare a quantity of normal carbonate of ammonium by saturating a solution of the commercial sesquicarbonate with ammonia-water and filtering the mixture after it has been allowed to stand for some time. Add the carbonate of ammonium solution, little by little, to the boiling solution of chloride of barium as long as any precipitate continues to fall. After the mixture has been allowed to settle decant the clear liquor and wash the precipitate 5 or 6 times by decantation with hot water, then throw it upon a filter and wash until the wash water acidulated with nitric acid no longer gives any precipitate when tested with nitrate of silver. Wash the precipitate out of the filter into a beaker and keep it for use, either in the moist state or air-dried.

Principle V. Power of decomposing refractory silicates, aluminates and chromites, when intensely heated.

Applications. Conversion of insoluble silicic acid into the soluble modification, in the analysis of some refractory siliceous minerals. Decomposition of spinel and other native aluminates, and of chrome iron ore, as a preliminary to their solution in acids. Decomposition of silicates as a preliminary to the estimation of alkali-metals.

Method A. For decomposing aluminates and chromites. Mix the finely powdered mineral with from 4 to 6 times its weight of pure, precipitated carbonate of barium, in a platinum crucible. Place the platinum crucible inside a somewhat larger crucible of refractory fire-clay; fill the space between the two crucibles with magnesia, cover the clay crucible and heat it intensely in a Sefström furnace during half or three-quarters of an hour.

Instead of the Sefström furnace, a powerful gas furnace, such as that of Griffin or of Grove, may be used to heat the naked platinum crucible. Or Deville's (*Annales Chim. et Phys.*, 1856, 46, 182) oil of turpentine furnace may be used. But in any event an intense heat is required to effect the fusion of the mixed aluminate and carbonate of barium. The heat of an ordinary wind furnace is insufficient for the purpose. — After the crucibles have been taken from the fire and allowed to cool, clean the outside of the platinum crucible and press it gently between the fingers to loosen the solid lump within it. Put the lump in a beaker, together with the crucible, if any portion of the fused mass still adheres to it, cover the mass with 10 or 15 times its bulk of water, and add strong chlorhydric or nitric acid, little by little, until solution is complete. Since all the carbonic acid of the carbonate of barium has been expelled by the intense heat, the fused mass will dissolve without effervescence; but care must be taken not to add too large a quantity of chlorhydric acid

at any one time, since the chloride of barium formed is only sparingly soluble in acid, and is liable to form an encrustation upon the mass which would impede its solution. (Abich, *Poggendorff's Annalen*, 1831, 23, pp. 319, 338). The action of fused carbonate of barium, or rather of the oxide of barium, into which the carbonate is converted at a high heat, is exceedingly energetic. Even the most refractory minerals may be readily and completely decomposed by means of it. According to Abich (*loc. cit.*, pp. 339, 341), even chrome iron ore may be completely decomposed by fusing it once or twice during three quarters of an hour with 4 parts of carbonate of barium.

Method B. For decomposing silicates, less carbonate of barium and a lower degree of heat will be required than are necessary for success in the applications of Method A. According to Deville (*Annales Chim. et Phys.*, [3.] 38, 5), 0.8 part of carbonate of barium is sufficient at a moderate red heat, to reduce 1 part of potash feldspar to the condition of a vitreous transparent mass, decomposable by acids.

The use of a larger proportion of carbonate of barium may even be injurious, since a portion of the potash set free by the caustic baryta formed, might be lost through volatilization. — In other respects the details of the process are similar to those described in A. It has been superseded in great measure, by the process of decomposing with fluorhydric acid, and by L. Smith's process with Carbonate of Calcium and chloride of ammonium. (See further under Silicates, and Oxide of Barium).

L. Smith's (*American Journ. Sci.*, 1853, 16, 53) old method of fusing silicates with a mixture of carbonate and chloride of barium will be described under the head of Silicates.

Principle VI. Insolubility in an aqueous solution of cyanide of potassium.

Applications. Separation of Ba from Co, Ni and Zn.

Method. See Carbonate of Cobalt.
Basic Carbonate of Bismuth.

Principle I. Insolubility in water and in solutions of alkaline carbonates.

Applications. Estimation of bismuth in compounds soluble in nitric acid and free from any admixture of other acids. Separation of Bi from Mn. Separation of Bi from Cu.

Method A. Add a very slight excess of carbonate of ammonium to the bismuth solution, heat the mixture nearly to boiling for a short time, filter, and ignite with the precautions prescribed under Carbonate of Lead. Weigh as Oxide of Bismuth. — The bismuth solution must not be too concentrated. If on diluting it with water, some basic nitrate of bismuth falls, no notice need be taken of it. The process is inapplicable, however, in presence of sulphuric or chlorhydric acids, since the precipitated carbonate and the ignited oxide would then contain an admixture of basic sulphate or basic chloride of bismuth. The mix-

ture of bismuth solution and carbonate of ammonium must always be heated in order to ensure complete precipitation. The results are in any event a trifle too low, for carbonate of bismuth is not absolutely insoluble in a solution of carbonate of ammonium.

Method B. To separate bismuth from copper, mix the nitric acid solution with an excess of carbonate of ammonium. Most of the copper remains dissolved in the excess of the ammonium salt, but a little of it is retained by the precipitated carbonate of bismuth. The precipitate must therefore be re-dissolved once or twice in nitric acid, and re-precipitated with carbonate of ammonium, in order to remove the last traces of copper. It is well to add some carbonate of ammonium to the water used for washing the precipitate. If these precautions be attended to, it is easy to remove all the copper from the precipitate (R. Schneider, *Journ. prakt. Chem.*, 60, 311), but a little bismuth always remains dissolved in the carbonate of ammonium and passes into the filtrate (H. Rose, *Pogg. Ann.*, 110, 430), hence the process is less accurate than that which depends on the insolubility of basic Chloride of Bismuth.

To estimate the copper, heat the ammoniacal filtrate, first by itself and afterwards with caustic lye, and collect the Oxide of Copper which is thrown down.

For the method of separating Bi from Mn, see Carbonate of Manganese.

Properties. When an excess of carbonate of ammonium is added to a nitric acid solution of bismuth, in the cold, a white precipitate of the monocarbonate ($\text{Bi}_2\text{O}_3, \text{CO}_2$) is immediately thrown down, but the precipitation is incomplete, since a portion of this monocarbonate remains dissolved in the ammonium salt. But on heating the mixture a more difficultly soluble basic salt is formed. Carbonate of potassium also precipitates bismuth completely, but the precipitate in that case retains traces of potash which are hard to wash out. The precipitate obtained by carbonate of ammonium is easily washed. It is as good as insoluble in water, but dissolves readily in acids. When ignited it gives off carbonic acid and is converted into teroxide of bismuth.

Principle II. Insolubility in an aqueous solution of cyanide of potassium.

Applications. Separation of Bi from Cu, Cd, Hg, Ag and Au.

Method. Add to the dilute solution a very slight excess of carbonate of sodium, then add an excess of a solution of cyanide of potassium, heat the mixture for some time, and collect the carbonate of bismuth upon a filter. Since the carbonate thus thrown down always retains some alkali, it must be dissolved in acid and re-precipitated. The cyanide of potassium used must be free from any trace of sulphide. (Fresenius & Haidlen, *Annal. Chem. und Pharm.*, 43, 129).

Carbonate of Cadmium.

Principle I. Insolubility in water and in carbonate of ammonium.

Applications. Estimation of cadmium in general. Separation of Cd from Mn and Cu.

Method A. Same as that described under Carbonate of Zinc. The precipitate should be collected upon a thin filter to avoid loss through reduction and volatilization, when the precipitate comes to be converted into Oxide of Cadmium.

Method B. In case cadmium is to be separated from copper, add carbonate of ammonium in excess, instead of the carbonate of sodium employed in Method A. Some cadmium will remain dissolved with the copper for a while, but on leaving the mixture exposed to the air all the carbonate of cadmium will gradually be deposited as carbonate of ammonium evaporates. (Stromeyer). The method is said to be more convenient but less accurate than those which depend upon the insolubility of Sulphide of Cadmium in cyanide of potassium, and its solubility in dilute sulphuric acid. It is distinctly inferior also to the method by Sulphocyanide of Copper.

For the method of separating Cd from Mn, see Carbonate of Manganese.

Properties. Carbonate of cadmium is a white precipitate, insoluble in water and the fixed alkaline carbonates; exceedingly sparingly soluble in a solution of carbonate of ammonium, but readily soluble in solutions of the sulphate, nitrate, etc., of ammonium. The water which the precipitate contains is completely expelled by drying, and the carbonic acid by ignition.

Principle II. Solubility in an aqueous solution of cyanide of potassium.

Applications. Separation of Cd from Bi and Pb.

Method. See Carbonate of Bismuth and Sulphide of Cadmium.

Carbonate of Calcium.

Principle I. Fixity when gently heated.

Applications. Estimation of calcium in oxalate of calcium and other compounds of calcium with organic acids.

Method. In case the substance to be operated upon is oxalate of calcium, heat it carefully and gradually in a platinum crucible until the bottom of the crucible has become almost, but not quite, dull red. The crucible should be covered at first, but may be open afterwards. Keep the crucible at this temperature, decidedly below incipient redness, during 8 or 10 minutes, then allow it to become cold, and weigh. — The carbonate of calcium obtained should be white, or only faintly tinged with gray. It should give no alkaline reaction when moistened and subsequently tested with a small slip of turmeric paper. If the turmeric turn brown it will be evident that the precipitate has been overheated and that a portion of it has been changed to caustic lime through es-

cape of carbonic acid. In that event pour as much of a strong aqueous solution of carbonate of ammonium into the crucible as will barely cover the precipitate, evaporate to absolute dryness upon a water bath, heat the dry precipitate gently over a lamp, but not nearly to redness, and again weigh. It is to be observed that a very moderate heat will be sufficient to volatilize the excess of carbonate of ammonium. There is no need of actually igniting the precipitate before weighing it the second time, and consequently no risk of expelling any carbonic acid from the revived carbonate. The process gives good results when properly conducted, but the operator should on no account fail to apply the test with turmeric paper. — Before proceeding to ignite oxalate of calcium, or carbonate of calcium which has been thrown down as such, take care to remove the precipitate from the filter as completely as possible, and burn the filter thoroughly upon the lid of the crucible out of contact with the precipitate. It is even best not to add the siliceous filter ash to the carbonate in the crucible until after the latter has been heated.

If any other salt than the oxalate is to be converted to the state of carbonate by ignition, proceed as directed under Carbonate of Barium (fixity of), and take special pains in treating the residue with carbonate of ammonium as above described.

Properties. Carbonate of calcium undergoes no change in the air at temperatures below faint redness, but at an intense red heat it gradually loses carbonic acid, especially when exposed to a current of air or steam. When mixed with carbon the decomposition by heat is far more rapid, carbonic acid being reduced and given off in the form of carbonic oxide. Quantities of carbonate of calcium as large as half a gramme may easily be completely converted to quicklime by heating them in an open platinum crucible over an ordinary gas blast lamp; but Fresenius has found that the heat of a Berzelius spirit lamp is insufficient to effect this reduction. The composition of the salt is as follows, both in terms of molecules and per cents.

$$\begin{array}{r} \text{CaO} = 56 \\ \text{CO}_2 = 44 \\ \hline 100 \end{array}$$

Principle II. Sparingly soluble in water.

Applications. Estimation of calcium in aqueous solutions of calcium salts. Separation of Ca from Na, K, Mg, Mn. Estimation of carbonic acid in rocks, soils, waters, air, etc. Indirect separation of Ca from Ba and Sr.

Methods.

A. Estimation of Calcium in solutions of its salts. Saturate the moderately dilute solution with ammonia-water, add a solution of carbonate of ammonium in slight excess and let the mixture stand in a warm place for several

hours. Collect the precipitate on a filter, wash it with water containing some ammonia, dry and ignite, or rather heat, the precipitate, as directed above (Principle I). The process yields accurate results when the liquid in which the precipitate is formed contains no great quantity of ammonium salts. It is essential that the precipitate be washed with ammoniated water, as will be seen below, under "properties."

B. Separation of Ca from K, Na and Mg. See the similar heading under Carbonate of Barium. Much that is said in that place of the preference to be given to Sulphate of Barium might be said here of Oxalate of Calcium.

C. Separation of Ca from Mn. See Carbonate of Manganese. There is nothing peculiar in the process as applied to the separation of Ca from Mn, excepting that the ignited precipitate must be treated with carbonate of ammonium to revivify the reduced carbonate of calcium, as has been explained above. See Carbonate of Calcium (fixity of). Unless the proportion of calcium in the mixture is large, it will usually be best not to weigh as CaO , $\text{Mn}_2\text{O}_3 + \text{CaO}$, CO_2 —but to ignite strongly over a blast lamp and weigh as CaO , $\text{Mn}_2\text{O}_3 + \text{CaO}$. See Oxide of Calcium.

D. Indirect separation of Ca from Ba and Sr. See Carbonic Acid (volatility of,—methods by simple ignition and ignition with an acid salt).

E. Estimation of Carbonic Acid.

1. *Fresenius's method.* Prepare a quantity of dry pulverulent hydrate of calcium by slaking a quantity of recently burnt lime with water. Put a small portion of the hydrate into dilute chlorhydric acid to test whether it is free from carbonic acid. If no effervescence is seen, seal up a number of portions, each of 2 or 3 grms., of the hydrate in small glass tubes for future use. But in case the hydrate is found to contain any carbonic acid place it in a tube of hard glass and ignite it upon a combustion furnace, in a current of air free from carbonic acid; and afterwards seal up several small portions of it as before.

Put 2 or 3 grms. of the pure lime into a light flask of about 300 c. c. capacity, close the flask with a caoutchouc stopper and weigh it together with the stopper and the lime. Pour in enough of the mineral water, or other solution of carbonic acid, to nearly fill the flask, replace the cork, shake the mixture and again weigh. The difference between the two weighings gives the weight of the mineral water. Loosen the stopper and heat the contents of the flask for some time upon a water bath, in order that the amorphous carbonate of calcium at first formed may become crystalline. Without disturbing the sediment at the bottom of the flask, pour the clear liquid upon a small plaited filter and allow the filter to drain; then, without washing either filter or precipi-

tate, throw back the filter with its contents into the flask and determine the carbonic acid by decomposing the carbonate with an acid and collecting the Carbonic Acid in soda-lime, in the manner described on p. 91. — In case the mineral water contains an alkaline bicarbonate, it is well, after filling the flask, to add to the liquid enough chloride of calcium to decompose the bicarbonate. It is unnecessary to make any correction or allowance in this case, for the trifling solubility of carbonate of calcium in water. — The method is accurate, simple and expeditious, and is very much to be preferred to the old method of treating the mineral water with a mixture of chloride of calcium, or chloride of barium and ammonia-water, and afterwards weighing or titrating the precipitate. (Fresenius, *Zeitsch. analyt. Chem.*, 1863, 2. 56).

In case the mineral water to be examined is contained in a bottle, it may be transferred to the lime flask by means of a syphon, after the bottle and contents have been cooled to about 4°. If the water were poured directly from the bottle into the flask, some free carbonic acid might flow into the latter with the water.

Sometimes the process above given of weighing the mineral water, had better be dispensed with, and only the volume of the water determined.

Thus when water is collected at a spring by opening a large pipette, or a flask provided with two orifices (Mohr, *Annalen der Pharm.*, 1834, 11. 231 or *Titrimethode*, 1855, 1. 115), beneath the surface of the water and then closing and withdrawing the vessel with its contents, it is easy to determine the capacity of the pipette or flask beforehand, and to transfer its contents directly to the lime flask without need of further measurement.

2. *By precipitating with a mixture of chloride of calcium and ammonia.* See the similar heading under Carbonate of Barium, and below under Principle III.

3. *Pettenkofer's method.* See below, and under Carbonate of Barium, also.

Principle III. Power of neutralizing acids.

Applications. Estimation of calcium, of carbonic acid, and of most free acids (see Acidimetry).

Methods.

A. *Estimation of Calcium* (Compare Alkalimetry).

Pour upon the powder or the moist precipitate which is to be examined, a measured quantity of nitric or chlorhydric acid of known strength, taking care to use a little more acid than would be sufficient to dissolve the carbonate. To do this, place the carbonate in a flask and pour the acid slowly upon it from a burette in such manner that no portion of the liquid shall be thrown out of the flask by the escaping carbonic acid. In order to drive out the carbonic acid which remains dissolved in

the acid solution, heat the latter carefully until it boils, then add a few drops of litmus, and determine the amount of free acid by titrating with a standard solution of soda. Or, better, omit the boiling and use Cochineal instead of litmus to indicate the point of saturation. By subtracting the amount of acid neutralized by the soda from the quantity of acid taken to dissolve the carbonate, the amount of acid neutralized by the latter will be obtained. The proportion of calcium in the precipitate, that is to say, the amount of calcium equivalent to the acid thus neutralized, may readily be calculated from these data.

B. *The estimation of Carbonic Acid* may evidently be effected in the same way as that of calcium, by the method just described, it being merely necessary to calculate how much carbonic acid is equivalent to the amount of standard acid neutralized by the carbonate.

The manner of applying the process will appear more fully in the following paragraphs.

C. *Pettenkofer's method of estimating carbonic acid by lime water.* Prepare a standard solution of oxalic acid of the strength indicated in the description of the analogous process with baryta-water (see Carbonate of Barium). Standardize a quantity of lime-water with this oxalic acid in the same way the baryta-water is standardized, and proceed with the analysis as follows:—Measure off 100 c. c. of the spring water or other dilute solution of carbonic acid to be analyzed, into a dry flask; add to it 3 c. c. of a highly concentrated solution of chloride of calcium, 2 c. c. of a saturated aqueous solution of chloride of ammonium, and 45 c. c. of the standard lime-water. Close the flask with a caoutchouc stopper, shake its contents, and leave it at rest for 12 hours in order that the amorphous carbonate of calcium, at first thrown down, may become crystalline. The total volume of liquid in the flask amounts to 150 c. c. Take out two portions, each of 50 c. c. of the clear liquid, and by means of the standard oxalic acid and turneric paper, determine in each portion how much hydrate of calcium still remains free and uncombined with carbonic acid. Precisely as in the operation of standardizing, the experiment upon the first portion of liquid will give an approximation to the truth, and that with the second portion an accurate result. Multiply by 3 the number of c. c. of oxalic acid used in the last experiment and subtract the product from the number of c. c. required to neutralize 45 c. c. of the standard lime-water. The difference will show how much lime has been precipitated by carbonic acid, and, as has been said, each c. c. of the acid corresponds to 1 millig. of CO_2 .

The chloride of calcium is added in the case of a mineral or spring water, as supposed above, to decompose any traces of carbonate or other alkaline salt whose acid might be precipitated by lime-water. The purpose of the chloride of ammonium, on the other hand, is to prevent the

precipitation of magnesium in case any compound of that metal be present. The addition of chloride of calcium is beneficial, moreover, in case the lime-water happens to contain traces of free caustic alkali, or the carbonic acid water any carbonate of magnesium, for, in the absence of chloride of calcium, an oxalate of either of the alkali metals or of magnesium would react upon the carbonate of calcium, which is almost always contained in carbonic acid waters, to form oxalate of calcium and a carbonate of an alkali or of magnesium, and the latter would immediately combine again with oxalic acid.

If the water under examination contains nothing but carbonic acid, it is merely necessary to add lime-water (or better, dilute baryta-water) to it, and heat the mixture for some time to 70° or 80° to facilitate the change of the amorphous carbonate to the crystalline condition, but in case any chloride of ammonium has been added to the mixture no heat should be applied lest some ammonia be expelled.

This process was formerly recommended by its author for the analysis of waters containing but little carbonic acid, while the analogous method with baryta-water was preferred for analyzing waters highly charged with carbonic acid. In his later papers, however, Pettenkofer urges that the process with baryta-water be always used, to the exclusion of lime-water, for the amorphous carbonate of calcium which forms when lime-water and carbonic acid are first mixed is somewhat soluble in water, and exhibits an alkaline reaction which may easily vitiate the titration. In presence of an excess of lime-water the amorphous carbonate of calcium changes to the insoluble crystalline state comparatively slowly. Baryta, moreover, exhibits a stronger alkaline reaction than an equivalent quantity of lime.

D. Old method of collecting carbonic acid in a mixture of chloride of calcium and ammonia. All that has been said under Carbonate of Barium of the preparation of the absorbent solution and the precipitation of the carbonic acid, applies here as well, with the exception that chloride of calcium must be substituted for the chloride of barium. There is, however, in this case no need of bringing the whole of the precipitate upon the filter, nor of rubbing off those portions of it which remain sticking to the flask. After the precipitate has been thoroughly washed, put the funnel which holds the filter into the neck of the flask in which the precipitate was formed, push a glass rod through the point of the filter and wash as much of the precipitate as possible from the filter into the flask, then spread out the filter upon a plate of glass, wash off the last particles of the precipitate into the funnel and flask, and boil the wash water gently for half an hour. The purpose of the boiling is to expel ammonia, some of which is retained by the precipitate even after long continued washing.

Pour into the flask a measured quantity of standard nitric or chlorhydric acid, more than sufficient to dissolve the whole of the precipitate, heat the liquid to expel the carbonic acid and titrate the excess of acid with a standard alkali, as described under Alkalimetry. The point of saturation may be indicated either by Litmus solution added to the liquor, or by Turmeric paper as in Pettenkofer's process above described.

According to Mohr, the alkalimetric process with carbonate of calcium is to be preferred to the corresponding process with carbonate of barium, in spite of the fact that carbonate of barium is more nearly insoluble in water than the calcium salt, for precipitated carbonate of calcium is far less bulky than carbonate of barium, and is more readily filtered than the latter, since it is less liable to clog the pores of filter paper. The comparatively high atomic weight of carbonate of barium has no significance in a process where the precipitate is not to be weighed. Like the carbonate of barium process, however, the method of precipitating carbonate of calcium from an ammoniacal solution is exposed to several sources of error, and is no longer held in much esteem.

In case of need, the process may be applied to the estimation of gaseous carbonic acid. In that event, the details of the method remain unchanged, with the exception that the gas is made to flow into a mixture of chloride of calcium and ammonia-water, or better, into ammonia-water to which chloride of calcium is afterwards added.

Properties of Carbonate of Calcium. The precipitate as ordinarily obtained, is a soft, white powder, scarcely at all soluble in absolutely pure, cold water, but appreciably soluble in ordinary distilled or other water which contains traces of carbonic acid gas, and the solution thus obtained exhibits a faint alkaline reaction. It is somewhat more readily soluble in boiling than in cold water. It is far from being insoluble in cold aqueous solutions of ammonium salts, such as the nitrate and chloride, and dissolves readily in hot solutions. The presence of free ammonia and carbonate of ammonium, however, hinders the solvent action of the ordinary ammonium salts. Solutions of the normal salts of potassium and sodium have a tendency to dissolve it, but their action is more feeble than that of ammonium salts. Carbonic acid water dissolves it easily. It cannot be precipitated from solutions which contain citrates or metaphosphates of the alkalis. (See, further, Dictionary of Solubilities).

For use as a reagent, pure carbonate of calcium may be prepared as follows:—Dissolve a quantity of white marble or of ignited stalactite, in chlorhydric acid, neutralize the solution with ammonia-water, heat the mixture to boiling and filter to separate the small quantity of iron and alumina which is thrown down. Heat the filtrate to boiling in a large beaker,

and throw into it, one by one, small bits of solid carbonate of ammonium until they cease to dissolve. Wash the heavy crystalline precipitate by decantation with hot water. (Matthiessen).

Principle IV. Power of precipitating iron, aluminum, manganese, chromium, etc. See the Hydrates of those metals. For lists of the substances precipitable by carbonate of calcium see that substance in Dictionary of Solubilities.

Principle V. Insolubility in an aqueous solution of cyanide of potassium.

Applications. Separation of Ca from Co, Ni and Zn.

Method. See Carbonate of Cobalt.

Principle VI? For the use of carbonate of calcium, or rather, of oxide of calcium, in decomposing silicious minerals, see Silicates.

The following account of *Lawrence Smith's method of separating alkalis* from refractory silicates by decomposing the mineral with carbonate of calcium and chloride of ammonium, is taken from Prof. Johnson's edition of *Fresenius's Quant. Analysis*, New York, 1870, p. 303. Though out of place in this connection, the importance of the process is such that early mention should be made of it. — Mix 1 part of the pulverized silicate with 1 part of dry crystallized chloride of ammonium by gentle trituration in a smooth mortar, then add 8 parts of pure, precipitated carbonate of calcium, and mix the whole intimately. Transfer the mixture to a platinum crucible, taking care to rinse the mortar with a little carbonate of calcium. Warm the crucible gradually over a small Bunsen burner until fumes of ammonium salts no longer appear; then heat to full redness, but not too intensely, during 30 or 40 minutes. An ordinary portable furnace or chafing dish provided with a conical sheet-iron cap or chimney 2 or 3 feet high will give heat enough for the purpose, in default of a large Bunsen lamp. — The mass in the crucible should sinter together but not fuse. When cold, it may usually be detached with ease from the platinum. Heat the sintered lump to boiling in a capsule with 100 c. c. of water for several hours, or until it is entirely disintegrated and fallen to powder. In case the lump, from having been overheated, remain partially coherent after long boiling, it may be transferred to a porcelain mortar, ground to fine powder and then boiled as before. Some silicates, notably those containing much protoxide of iron, fuse easily with the proportions of flux above given. It is best when this happens to repeat the ignition on a new quantity of the mineral, using as much as 10 or 12 parts of carbonate of calcium and taking care to bring only the lower three-fourths of the crucible to a red heat. — When completely disintegrated by boiling with water, the sintered mass gives up to the water all the alkalis as chlorides, together with some chloride of cal-

cium and caustic lime. The mixture is filtered and the powder well washed; a quantity (1 or 2 grms.) of carbonate of ammonium in solution is then added to the filtrate and the latter is evaporated to a bulk of about 30 c. c. A little more carbonate of ammonium together with a few drops of ammonia-water is added to ensure a complete separation of the calcium, and the mixture is again filtered. Collect the filtrate and washings in a weighed platinum capsule and evaporate to dryness on a water bath. Place the capsule in a capacious iron cup and heat the latter so that the contents of the platinum capsule within it may be thoroughly dried. Finally, heat the capsule carefully almost to redness to drive out the ammonium salts, cool and weigh. The alkali chlorides thus obtained are nearly pure, though a trifling amount of black residue will usually be seen on dissolving them in a few drops of water. This residue may be removed, if need be, by filtering through a very small filter. — Prof. Smith's process is by far the most convenient and accurate for separating the alkalis from silicates, and is universally applicable except perhaps in presence of boracic acid. (Johnson, *loc. cit.*).

BiCarbonate of Calcium.

Principle. Power of neutralizing acids.

Application. Estimation of bicarbonate of calcium in natural waters.

Method. The method is merely one of Acidimetry, in which a solution of phosphate of copper in chlorhydric acid is made to serve both as the standard acid and as the indicator of the point of saturation. — To prepare the copper solution, mix a solution of cupric chloride with one of ordinary phosphate of sodium, wash the phosphate of copper which is precipitated, mix the washed precipitate with water, and add to the mixture moderately strong chlorhydric acid, drop by drop, until the chlorhydric acid being slightly in excess, a clear solution is obtained. When such a solution is dropped into a solution of bicarbonate of calcium—or of any carbonate or bicarbonate of either of the alkali—or alkaline—earthy metals—a quantity of the phosphate of copper is precipitated, at first, as the calcium, or other alkaline metal, neutralizes the free chlorhydric acid; but the liquid soon becomes clear again when a further portion of the cupric solution is added, for the precipitate redissolves in the free acid which this solution contains. — The moment at which the turbid solution becomes clear, is taken as the point of saturation, for the quantity of cupric solution required to effect the precipitation and re solution is proportional to the amount of base in the substance tested, and consequently to the amount of carbonic acid which was combined with the base to form a bicarbonate. The presence of free carbonic acid, that is to say, of an excess of the acid over and above what is necessary to form a bicarbonate, has no influence whatever upon the indications of

the process. — The cupric solution is standardized against pure, dry carbonate of sodium. To this end dissolve 0.265 grm. (equal one two-hundredth of an equivalent), of the dry salt in distilled water, dilute the solution to the volume of a litre (see Alkalimetry), and saturate the solution with carbonic acid gas. The copper solution may be made of such strength that 4.4 c. c. of it will saturate, in the manner explained above, 100 c. c. of the standard soda solution. With a liquid of this strength, it will only be necessary to multiply by $22 \div 44$ ($= 0.5$) the number of c. c. of the liquid consumed in titrating any 100 c. c. sample of natural water, in order to obtain the amount of carbonic acid in that water expressed in terms of centigrammes. It is well also to employ a burette graduated to fifths of cubic centimetres. — The process is said to be superior to that of Barthélemy (see Carbonate of Mercury), inasmuch as it is applicable to waters contaminated with chlorides and sulphates. It succeeds better with bicarbonates than with the normal carbonates, and may be applied to either of the bicarbonates as well as to bicarbonate of calcium. (Lory, *Chemical News*, 18. 169).

Carbonate of Cobalt.

Principle I. Solubility in an aqueous solution of cyanide of potassium.

Applications. Separation of Co from Ba, Sr, Ca and Al.

Method. Mix the solution with a slight excess of carbonate of sodium. Add a quantity of cyanide of potassium solution to the mixture of liquid and precipitate, and heat the whole gently until the whole of the carbonate of cobalt has redissolved. Collect the undissolved carbonate of the alkaline earths upon a filter, and precipitate the cobalt in the filtrate as Cobaltcyanide of Mercury.

Principle II. Insolubility in water.

Carbonate of cobalt may be precipitated by adding an alkaline carbonate to the solution of a cobalt salt. But the precipitation, can with difficulty be made complete even by long continued boiling. The principle is not to be recommended as a means of determining cobalt. (Gibbs & Taylor, *American Journ. Sci.*, 1867, 44. 214).

Carbonate of Cobalt and of Calcium.

Principle. Insolubility.

Application. Separation of Co from Ni.

Method? Dissolve the mixture of cobalt and nickel in a slight excess of chlorhydric acid and add to the solution 10 parts of chloride of calcium and 10 parts of chloride of ammonium for every 3 parts of the mixed oxides which are contained in it. Mix the solution with 150 parts of cold water and 20 parts of sesquicarbonate of ammonium, previously dissolved in 100 parts of cold water, and gradually heat the mixture to boiling. After the solution has been allowed to cool and settle,

collect the precipitate upon a filter and wash with a solution of carbonate of ammonium. To estimate the cobalt, dissolve the mixed precipitate in chlorhydric acid and proceed in the usual way. The nickel may be determined in the filtrate. (L. Thompson, *Zeitsch. analyt. Chem.*, 1864, 3. 375). Experiments by Winkler, *ibid.*, p. 376, go to show that the process as presented by Thompson, is wholly unfit for quantitative use. Not only is some carbonate of nickel always found in the precipitate, but a quantity of cobalt invariably remains in solution and passes into the filtrate.

Carbonate of Copper.

Principle I. Solubility in an aqueous solution of carbonate of ammonium.

Applications. Separation of Cu from Bi and Cd.

Method. See the Carbonates of Bismuth and of Cadmium.

Principle II. Solubility in an aqueous solution of cyanide of potassium.

Applications. Separation of Cu from Bi and Pb.

Method. See Carbonate of Bismuth and Sulphide of Copper.

Principle III. Insolubility of the basic carbonate.

Applications. Estimation of copper in acid solutions. Separation of Cu from Mn.

Method. Some years since, H. Rose (*Handbuch analyt. Chem.*, 1851, 2. 188) stated that copper cannot be completely precipitated by means of carbonate of potassium. According to this chemist a certain proportion of the copper remains obstinately in solution, and can only be obtained by evaporating the liquid to dryness and gently igniting the residue. But Gibbs has found that Rose's statement is too strong; the whole of the copper may be precipitated by alkaline carbonates from solutions of sulphate, nitrate or chloride of copper when the latter are sufficiently dilute and are boiled for a long time with the carbonated alkali.

The best method of effecting the precipitation is as follows:—Dilute the copper solution until it contains no more than one gramme of copper to the litre. Add a solution of carbonate of potassium or of sodium, in slight excess, and boil the mixture for half an hour. The boiling proceeds quietly without bumping; the blue-green carbonate soon becomes dark brown and the oxide or basic carbonate finally obtained has a fine granular character which renders it extremely easy to wash. The small portion of the precipitate which usually adheres to the sides of the vessel in which the boiling takes place, must be redissolved in acid and again precipitated; but great care must be taken not to add too large an excess of the alkaline carbonate, lest a solution be formed from which the copper cannot be precipitated by boiling. If the process be well conducted, the original filtrate will be perfectly free from copper. The washed precip-

itate may be ignited in a current of hydrogen, and the Copper weighed as such; it will be found to be free from alkali. The ignition must be carefully conducted, since the ignited precipitate is so finely divided that particles of it are liable to be carried off in the current of gas. (Gibbs & Taylor, *American Journ. Sci.*, 1868, 44. 213).

For the method of separating Cu from Mn, see Carbonate of Manganese; as well as the description above given. Test the filtrate from the mixed carbonate with sulphhydrate of ammonium, to be sure that all the copper has gone down.

Carbonate of Lead.

Principle I. Insolubility in cold water.

Applications. Estimation of lead in all salts of that metal which are soluble in water, or from which the lead can be dissolved by nitric acid. Separation of Pb from Mn.

Method. Add a slight excess of carbonate of ammonium, together with a small quantity of ammonia-water, to the moderately dilute solution of the lead salt. Heat the mixture for some time, and allow it to settle until the liquid has become clear, then collect the precipitate upon a small, thin filter and wash it with cold water which has been recently boiled to expel carbonic acid. Ignite the dried precipitate in a porcelain crucible and weigh as Oxide of Lead. The filter should be burned by itself upon the cover of the crucible, after the precipitate has been removed from it as completely as possible. It is well also to moisten the cold filter-ash with a drop or two of nitric acid, and to evaporate and ignite before weighing. — The process is a tolerably satisfactory one, though the results obtained are usually somewhat too low, on account of the solubility of the precipitate. It is easy to incur loss also in burning the filter, through reduction of some of the precipitate left upon the paper. The method, however, is better than that which depends on the insolubility of Oxalate of Lead. (Mohr and Fresenius).

Lead may be precipitated as completely by means of the bicarbonate of potassium or sodium as by carbonate of ammonium; normal carbonate of lead being thrown down in both instances. But the precipitation is not complete with the normal alkaline carbonates, and a not insignificant portion of the precipitate may be dissolved in case it is heated with an excess of the normal carbonate of either of the fixed alkalis. (H. Rose).

For the separation of Pb from Mn see Carbonate of Manganese. Add carbonate of ammonium or bicarbonate of sodium to the filtrate from the mixed carbonates of Pb and Mn, to ensure the complete precipitation of the lead.

Properties. Precipitated carbonate of lead is heavy, white and pulverulent. It is almost absolutely insoluble in water which contains

no trace of carbonic acid, but dissolves in carbonic acid water. According to Fresenius, 1 part of it dissolves at the ordinary temperature in about 50,000 parts of water which has been boiled. It is more soluble in water charged with ammoniacal salts than in pure water. On ignition it loses its carbonic acid readily. When thrown down by an excess of bicarbonate of sodium the precipitate retains traces of the sodium salt.

Principle II. Insolubility in an aqueous solution of cyanide of potassium.

Applications. Separation of Pb from Cu, Cd, Hg, Ag and Au.

Method. See Carbonate of Bismuth. The carbonate of lead thus precipitated always contains alkali. It may be dissolved in nitric acid and reprecipitated by carbonate of ammonium, as in Principle I, or as Sulphate of Lead. Or it may be reduced to metallic Lead by fusion with cyanide of potassium.

Basic Carbonate of Magnesium.

Principle I. Insolubility in water.

Applications. Estimation of Mg in presence of K, and in a solution of Mg in carbonic acid water. (Method A). — Separation of K from a mixture of Mg, Ba and Ca. (Method B). — Separation of Mg from Mn.

Method A. To estimate magnesium in presence of alkalis, when the quantity of the latter is not to be determined, boil the solution strongly for a long time with an excess of carbonate of potassium, and wash the precipitate with boiling water. The washing must be proceeded with without interruption until a few drops of the filtrate leave only a small residue when evaporated on platinum foil. Though the compound is somewhat soluble in water, it is less so in hot than in cold, and comparatively little of it is taken up by water which is boiling hot and free from carbonic acid. The dried precipitate is ignited strongly and the residue weighed as Oxide of Magnesium. — This method was formerly much employed, but is no longer held in esteem. It is inconvenient and liable to several sources of error. Hence it has been superseded by the method which depends on the insolubility of Phosphate of Magnesium and Ammonium. The normal carbonate of magnesium, which may be supposed to be precipitated at the moment when carbonate of potassium is added, is decomposed, by boiling, into an insoluble basic and a soluble acid carbonate, and in order to decompose the latter completely the liquor has to be boiled for a long time. A similar remark applies to the case where magnesium is to be determined in a carbonic acid water solution. — The mixture must be boiled strongly from first to last, in order to avoid a difficultly soluble compound of carbonate of magnesium and carbonate of potassium, which forms at moderate heats. Carbonate of sodium is somewhat inferior to carbonate of potassium as the precipitant, since an insoluble

double carbonate forms more readily with sodium than potassium. Both these double compounds are decomposed by ignition, or rather, after ignition it is easy to wash out the alkaline carbonate from the oxide of magnesium. — Since it is not easy to determine when all the magnesium has been precipitated, and since some of it would inevitably remain dissolved if the boiling were stopped too soon, it is well to evaporate the liquid to dryness in order to be sure that the separation is complete. To this end let the boiled mixture settle, decant the clear liquor into an evaporating dish, best of platinum, throw the precipitate upon a filter and add the filtrate and first portions of wash water to the liquid in the dish. Boil down the liquid rapidly to absolute dryness, heat the residue strongly, and after the dish has become cold treat the residue with hot water. Collect the small portion of the mass that remains undissolved, upon a small filter, and wash it by itself. To avoid loss in the process of drying, place the dish, at last, within a capacious iron cup and stir its contents continually, at a gentle heat, until the mass is completely dry. The liquid must be boiled strongly during the process of evaporation in order to hinder the saline matter from creeping over the edge of the dish. The original method of evaporating the entire mixture of precipitate and liquid to dryness is not to be commended. (v. Bonsdorf, *Pogg. Annal.*, 18. 128). — In case the magnesium solution contains ammonium salts, carbonate of potassium must be added to destroy them. A large excess of carbonate of potassium is added to the liquid, the mixture is warmed until the odor of ammonia ceases to be perceptible, more carbonate of potassium is added, and the mixture again warmed to make sure that the whole of the ammonia has been expelled, and the liquid is finally boiled as above described. In case the boiled liquid fails to give a strong alkaline reaction with red litmus paper, a new quantity of carbonate of potassium must be added, and the mixture again boiled. (H. Rose, *Handbuch*, 1851, 2. pp. 33–37, 52).

Method B. Heat the chlorhydric acid solution of magnesium, calcium, barium and the alkalis to actual boiling, add a solution of carbonate of sodium, drop by drop, as long as any precipitate continues to fall, and boil strongly until the voluminous precipitate becomes compact and granular. If the precipitate is boiled long enough it can be washed free from potassium. Acidulate the filtrate with chlorhydric acid, and determine the potassium as Chloroplatinate of Potassium. (Stohmann, *Zeitsch. analyt. Chem.*, 1866, 5. 307).

For the method of separating Mg from Mn, see Carbonate of Manganese.

According to Bineau, 1 litre of water dissolves 0.06 grm. of three-fourths carbonate of magnesium. According to Chevalet, a litre

of water dissolves 0.106 grm. of normal (?) carbonate of magnesium. (*Zeitsch. analyt. Chem.*, 1869, 8. 91).

Principle II. Solubility in carbonic acid water.

Applications. Separation of Al from Mg and from both Mg and Ca, if the proportion of the latter be very small.

Method. Place the cold, moderately acid, rather dilute solution in a beaker provided with a suitable cover. Add a solution of bicarbonate of potassium or sodium prepared in the cold, as long as any effervescence occurs, or any precipitate falls. Violent effervescence occurs during the precipitation, all the alumina is thrown down in the form of a hydrate, while the magnesium remains dissolved in the liquid charged with carbonic acid. After the mixture has been allowed to stand for 12 hours, decant the clear liquid into a filter and wash the precipitate, first with cold carbonic acid water by decantation, and afterwards with pure water upon the filter. Carbonic acid water for the washing may be prepared by slowly adding to a highly dilute solution of bicarbonate of potassium or sodium a small quantity of chlorhydric acid, insufficient to combine with the whole of the metal. — Magnesium may be determined directly in the filtrate, as Phosphate of Magnesium and Ammonium. The alumina precipitate is often free or almost free from any trace of magnesium (H. Rose) but since it is liable to retain some alkali, it had better be dissolved in chlorhydric acid and the solution treated with ammonia-water to throw down Hydrate of Aluminum. — The process was formerly much employed and would still appear to be valuable.

In case the method is employed for separating both lime and magnesium from aluminum, the solution should be very dilute and a stoppered flask should be employed, instead of a beaker, to effect the precipitation. Satisfactory results can be obtained only when the quantity of lime is very small, since it is liable to be retained by the alumina.

Principle III. Power of neutralizing acids.

Application. Valuation of the commercial carbonate.

Method. Dissolve about a gramme of the substance to be tested in 60 or 70 c. c. of normal nitric acid, taking care to measure the acid and to use an excess of it. Determine the excess of acid by titration with a standard solution of ammonio-sulphate of copper (see Acidimetry), and subtract this excess from the amount of acid taken. The difference will be equivalent to the amount of magnesium in the substance. The results obtained are usually somewhat too low. The process is of technical application only; it has no claim to scientific accuracy. — Instead of the ammonio-sulphate of copper, standard ammonia-water may be employed to determine the excess of acid, but, according to Mohr, the copper solution is to be preferred.

In any event magnesium is less conveniently determined by alkalimetric methods than either of the metals of the alkaline earths. When normal nitric acid and litmus solution are added either to carbonate of magnesium or to calcined magnesite, the red color of the litmus very soon changes to blue and remains so as long as any trace of the magnesium compound is left undissolved. On adding more of the acid, until the color appears bright red, and then titrating backwards with caustic soda until the liquid becomes blue, results are obtained which indicate too little magnesium. (Mohr, *Titrimethode*, 1855, l. pp. 80, 357).

Principle IV. Decomposition of by solutions of ferric salts, while hydrate of iron is precipitated. (Compare the Carbonates of Barium and Calcium).

Application. Separation of Fe_2O_3 from FeO in sulphuric acid solutions.

Method. See Hydrate of Iron. In this process the normal carbonate (*magnesite*) must be employed. The basic carbonate (*magnesia-alba*) will not answer.

BiCarbonate of Magnesium.

(Compare *biCarbonate* of Calcium).

Carbonate of Magnesium and of Ammonium.

Principle. Sparing solubility in ammoniated water.

Application. Separation of magnesium from the alkalies.

Method. Prepare an exceedingly concentrated solution of the substance to be analyzed, and in case it be acid, neutralize, or slightly supersaturate it with ammonia-water. Add to the liquid a large excess of a solution of normal carbonate of ammonium which contains rather more than one equivalent of oxide of ammonium for each equivalent of carbonic acid. To prepare this solution dissolve 230 grms. of commercial, solid, sesquicarbonate of ammonium in 180 c. c. of ammonia-water of 0.92 sp. gr., and enough water to bring the solution to the volume of a litre. Stir the mixture strongly until the voluminous precipitate which falls at first, on the addition of the carbonate of ammonium has completely re-dissolved. Then leave the mixture at rest for 12 or 24 hours. Collect the crystalline precipitate upon a filter, wash it with the solution of normal carbonate of ammonium, dry, ignite, and weigh the Oxide of Magnesium. — In separating magnesium from sodium, the precipitate can readily be washed free from fixed alkali; but if potassium be present, some carbonate of potassium is retained by the precipitate so strongly that it can only be washed out after the precipitate has been ignited. The ignited magnesia must consequently be washed with hot water in case potassium is present.

It is not absolutely necessary that the precipitate first formed should be completely re-dissolved, since when left to itself in the liquid it gradually contracts and becomes crystalline;

but it is always safer to dissolve it by means of an excess of the precipitant and by agitation.

The final precipitate is granular and may be washed readily. It does not adhere firmly to the sides of the beaker. But the chief merit of the process consists in its applicability even in presence of large quantities of salts of ammonium or of the fixed alkalies. It is only necessary in that case to let the mixture stand for 24 hours and to stir it frequently. The process is inapplicable in presence of phosphoric or arsenic acids. (Schaffgotsch, *Pogg. Annal.*, 104. 482; H. Weber, *Kopp's Jahresbericht*, für 1858, p. 606).

The behavior of the double salt towards solvents has been studied in some detail by Divers, (*Journ. London Chem. Soc.*, 15. 196; *Zeitsch. analyt. Chem.*, 1. 474), who appears, however, to have been ignorant of the labors of Schaffgotsch and Weber. According to Divers, the solution of normal carbonate of ammonium may be made to contain 1 part of salt to 6 parts of water. About 4 equivalents of the carbonate of ammonium should be taken for each equivalent of magnesium to be precipitated; and one equivalent or more of chloride of ammonium should be mixed with the magnesium solution before adding the precipitant, in order to prevent the precipitation of any normal carbonate of magnesium. — The composition of the double salt is $\text{MgO}, \text{CO}_2, (\text{NH}_4)_2\text{O}, \text{CO}_2 + 4\text{H}_2\text{O}$. According to Schaffgotsch, 1 part of it requires 60,000 parts of a solution of normal or slightly alkaline carbonate of ammonium for its solution. It is somewhat soluble in a solution of chloride of ammonium, when no carbonate of ammonium is present. Divers found 1 part magnesia in 4660 parts of a mother liquor which contained an excess of carbonate of ammonium, some chloride of ammonium and a large quantity of sulphate of ammonium.

Carbonate of Manganese.

Principle. Insolubility in water.

Applications. Estimation of manganese in all salts of that metal which dissolve in water, excepting the salts of some fixed organic acids; and in all compounds from which the manganese can be dissolved out by chlorhydric acid. Separation of Mn from Ca, Ba, Sr, Mg, Al, Fe, Zn, Cd, Pb, Cu, Bi and P_2O_5 .

Method. Place the moderately dilute solution in a tolerably large beaker, cover the beaker with a watch-glass-shaped cover, at the centre of which a hole has been bored, and heat the liquid. Pour a solution of carbonate of sodium, drop by drop, through the cover of the beaker until it is slightly in excess, heat the mixture to boiling for a moment and afterwards allow it to settle until the liquid is clear. The original manganese solution should be slightly acid, but not too acid lest some of the liquid be lost through the violent evolution of carbonic acid gas. — In case the manganese solution contains any salt of ammo-

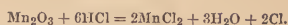
nium, a large excess of the alkaline carbonate must be employed, and the mixture be boiled down nearly to dryness, until no more fumes of ammonia escape, in order to ensure complete precipitation. The formation of dark colored oxide of manganese during the evaporation does no harm. During the evaporation the cover of the beaker must be taken off.

Wash the precipitate by decantation with boiling water, dry the precipitate and ignite and weigh as Manganite of Manganese (MnO , Mn_2O_3). In case the filtrate or wash water from the carbonate of manganese is not absolutely clear, let it stand 18 or 24 hours in a warm place and collect and wash the dirty brown precipitate upon a special filter. When carefully executed the process yields accurate results.

Properties. Recently precipitated manganous carbonate is a white flocculent substance, scarcely at all soluble in pure water, but somewhat soluble in water which contains carbonic acid. It is no more soluble in salts of the fixed alkalis than in water, but dissolves rather easily in ammonium salts. It cannot be completely precipitated in presence of ammonium salts, nor is it precipitable in presence of citric and other fixed organic acids. When left moist in the air, or when washed with water which contains air, the precipitate slowly takes on oxygen and becomes rusty through formation of hydrated sesquioxide of manganese. — When dried, out of contact with the air, the precipitate yields a white powder of the composition MnO , $CO_2 + \frac{1}{2} Aq$; but when dried in the air the powder is always more or less colored. When heated to redness in the air, the powder becomes black and afterward brown. By long continued ignition it is completely converted into MnO , Mn_2O_3 .

To separate either of the metals above enumerated from manganese, precipitate the latter together with the other metal by means of carbonate of sodium, as above described. Wash the mixed precipitate thoroughly, dry, ignite and weigh. The ignited precipitate consists of a mixture of MO , $Mn_2O_3 + x MO$, or of MO , $Mn_2O_3 + x (MO, CO_2)$, accordingly as the carbonate of M is or is not decomposed by ignition. In case the metal precipitated, together with the manganese, is iron or aluminum, all the manganese will be in the form of Mn_2O_4 . — Place a weighed portion of the ignited precipitate in a small flask, together with some pure concentrated chlorhydric acid. Heat the mixture, conduct the chlorine, which is evolved, into a solution of iodide of potassium and estimate the iodine, which is set free, by means of hyposulphite of sodium. Or estimate the Chlorine in any appropriate way. (Compare Manganites, and Manganite of Manganese.) In case the method with iodide of potassium be used, the amount of iodine found will correspond, atom for atom, to that of the chlorine set free from the chlorhydric acid.

But for every two atoms of chlorine evolved there must have been present one molecule of sesquioxide of manganese: —



To find the weight of the other metal deduct the weight of the sesquioxide of manganese from the total weight of the mixed precipitate, and, if need be, add to the difference the weight of the carbonic acid which was expelled by the manganese during the ignition. That is to say, for the metals Ba, Ca and Sr, which retain carbonic acid on ignition, allow one molecule of CO_2 for every molecule of Mn_2O_3 . — As thus far described, excepting the case of iron or aluminum, the method presupposes that more than one molecule of MO is present for every molecule of Mn_2O_3 , for if the proportion of MO were less than this the ignited precipitate would contain some MnO , Mn_2O_3 , as well as MO , Mn_2O_3 . The process may be made available, however, in all cases by the following modification: Weigh out half as much oxide of zinc at there is supposed to be MO and MnO in the mixture, dissolve it in chlorhydric acid, mix the solution with the substance to be analyzed and precipitate the whole with carbonate of sodium. The ignited precipitate will contain the whole of the manganese in the form of Mn_2O_3 . (Krieger, *Annal. Chem. und Pharm.*, **87**, 261).

To separate manganese from phosphoric acid. Fuse the weighed substance with carbonate of sodium for some time, boil the fused mass with water, add a little sulphuretted hydrogen water to reduce any manganic acid which may have formed, collect the insoluble carbonate of manganese upon a filter and wash, dry, and weigh, as above.

Carbonate of Mercury. (Mercurous carbonate).

Principle. Insolubility in water and solubility in nitric acid.

Applications. Estimation of carbonic acid in bicarbonates, especially as they occur in natural waters. Separation of bicarbonates of the alkalis from those of the alkaline earths. Use as an indicator in Acidimetry.

Method. Prepare a solution of acid mercurous nitrate by digesting an excess of quicksilver with dilute nitric acid, pouring off the mother liquor from the crystals of the basic salt, and diluting it with 4 or 5 parts of water. By leaving the solution in contact with metallic mercury it may be preserved for a long time. When this solution is added to dilute solutions of bicarbonates of the alkalis or alkaline earths, at temperatures lower than 30° , a precipitate falls which is white at first, but soon changes to yellowish-orange, or sometimes to yellowish-green. This precipitate dissolves in an excess of the acid mercurous nitrate, as well as in sulphuric and nitric acids and in organic liquids, such as urine. Precipitates obtained, under analogous conditions,

from the normal carbonates are brown and insoluble in an excess of the mercurous nitrate.

Prepare a standard solution of bicarbonate of potassium by dissolving 0.5 gm. of the bicarbonate in water to the volume of a litre. This quantity of the bicarbonate is equivalent to 0.241 gm. of carbonic acid. Standardize a quantity of the mercurous nitrate by pouring it, drop by drop, from a Gay-Lussac burette into measured portions of the standard solution of bicarbonate of potassium, until the precipitate which forms at first has completely redissolved. Repeat the titration two or three times with different quantities of the bicarbonate solution until the results agree. Then titrate the bicarbonate, or the water, to be tested, in the usual way. (See Acidimetry).

In order to separate alkaline bicarbonates from bicarbonates of the alkaline earths, proceed as above, with one portion of water to be tested. Then boil another portion of 100 c. until the carbonates of the alkaline earths have all been thrown down, filter, add water to the filtrate to replace what has evaporated, saturate the filtrate with carbonic acid and titrate with the mercurous solution to determine the proportion of alkaline bicarbonate. Or, add to a measured quantity of the water, a measured volume of standard caustic potash (0.5 gm. to the litre) sufficient to change the bicarbonates of the alkaline earths into neutral salts, let the mixture stand for several days, decant the clear liquid, saturate it with carbonic acid and titrate as before. Subtract, of course, the bicarbonate of potassium which has resulted from the caustic alkali employed.

The presence of sulphates or chlorides in the water interferes materially with the success of the process, but when the proportion of chlorine is not too large the bicarbonates can still be determined approximately, as follows:—Measure out several portions of 100 c. c. each, of the water, acidulate them with nitric acid, and observe about how many drops of the standard mercurous nitrate are required in order to precipitate the chloride and impart a definite gray coloration to the liquid. By trying several experiments it is easy to hit this point with sufficient accuracy. Then add the standard mercurous nitrate to a fresh, non-acidulated 100 c. c. portion of the water, until the yellowish-orange precipitate has disappeared and the liquid has acquired the gray coloration aforesaid. — Since the mercurous nitrate acts upon caoutchouc, it cannot be used with Mohr's burette unless the latter be provided with a glass cock or regulated by a clip at the top. (Barthélemy, *Zeitsch. analyt. Chem.*, 1869, 8. 91).

Carbonate of Nickel.

Principle I. Solubility in an aqueous solution of cyanide of potassium.

Applications. Separation of Ni from Ba, Sr, Ca and Al.

Method. Same as that described under Carbonate of Cobalt.

Principle II. Insolubility in water.

Method. Same as that described under Carbonate of Copper. The green basic carbonate of nickel, obtained by boiling the dilute solution of a nickel salt with an alkaline carbonate, may be washed much more readily than the precipitate obtained by means of a caustic alkali. According to Genth, the process yields highly satisfactory results. (Gibbs & Taylor, *American Journ. Sci.*, 1867, 44. 214).

Carbonate of Potassium. [Compare Carbonate of Sodium].

Principle I. Fixity of the salt at moderately high temperatures.

Applications. Estimation of potassium in many potassium salts of organic acids. Valuation of argol and cream of tartar.

Method. Heat the salt gently for a long time in a covered platinum crucible, until absolutely no more visible fumes escape. Wash out the black porous residue from the crucible into a beaker, cover the latter with a watch glass, and add dilute chlorhydric acid to the solution as long as there is any effervescence. Filter the acidulated liquor, to separate the particles of carbon, evaporate the filtrate in a platinum cup and weigh the Chloride of Potassium. Or, instead of chlorhydric acid, use dilute sulphuric acid, and weigh as Sulphate of Potassium. In some cases, as in the examination of tartar, it will be most convenient to estimate the potassium in the carbonate by the method of alkalimetry (see below, Principle II).

The carbonate of potassium in the crucible must never be heated to the point of fusion, and the crucible should be kept covered throughout the operation. If the crucible were left open and the residue roasted until it became white, a considerable quantity of carbonate of potassium would be lost through volatilization. A small proportion of the potassium is usually lost in this way during the process of carbonization, but the process nevertheless yields perfectly satisfactory results when properly conducted. If the process of heating be continued long enough a colorless solution will be obtained when the residue is treated with water. (Braun, *Zeitsch. analyt. Chem.*, 1868, 7. pp. 149, 150). See also Aug. Vogel (*ibid.* p. 149) for quantitative experiments, showing the large amount of carbonate of potassium which may be lost by volatilization. — It is not well to burn the coaly residue white by throwing in fragments of nitrate of ammonium (as directed by H. Rose), because of the great heat which would be produced by the combustion. Nor is it advisable to use nitric acid instead of chlorhydric, as the solvent of the carbonate.

In some rare cases it may be best to weigh carbonate of potassium as such, though, on ac-

count of its tendency to deliquesce, the salt is not well adapted for weighing. In that event, evaporate the solution to dryness in a platinum crucible and ignite the residuc at a moderate heat. A few small fragments of solid carbonate of ammonium may be placed in the crucible before the final ignition, in order to convert into carbonate of potassium any traces of caustic potash which may be present. It is to be observed that in igniting carbonate of potassium in contact with carbon, some of the carbonic acid is decomposed, carbonic oxide being set free and caustic potash produced. This decomposition occurs particularly when the carbonate of potassium is heated to fusion in contact with charcoal. The crucible in which carbonate of potassium is weighed should have a tight cover, to hinder the salt from absorbing water from the air during the operation of weighing. All trouble from deliquescence may be avoided, however, by igniting the carbonate with chloride or with sulphate of ammonium and weighing as Chloride or Sulphate of Potassium, as the case may be.

Principle II. Power of neutralizing acids.

Applications. Estimation of potassium in the commercial carbonate; in other words, valuation of pearlash, saleratus, potashes and wood ashes. Valuation of argol and cream of tartar.

Methods. The proportion of pure carbonate of potassium in any given sample of the commercial article may be estimated, either by determining how much of a standard acid can be neutralized by a weighed quantity of the sample (see Alkalimetry), or by determining how much carbonic acid is set free when a weighed quantity of the sample is mixed with a weighed quantity of acid or fused with an acid salt (see Carbonic Acid, volatility of, Methods C and B; also p. 22).

The commercial carbonates of potassium are liable to contain substances insoluble in water,—such as carbonate, silicate, and phosphate of calcium, sand, and dirt, which may be removed by filtration; and neutral salts, such as the alkaline chlorides and sulphates, which have no influence whatsoever in the process of titration. But, besides these harmless ingredients, there may be present certain other compounds,—such as the hydrate, silicate, phosphate, sulphite, sulphide and hyposulphite of potassium,—which must be guarded against in certain cases. [Compare Carbonate of Sodium]. — In many cases it will be sufficient to determine the amount of “available alkali” in the sample, without reference to its precise chemical composition. For example, if the commercial article under examination is to be used for making caustic potash by boiling the aqueous solution with lime, the presence of a small quantity of silicate or of phosphate of potassium will do no harm, any more than that of caustic potash, since both of these compounds will be made caustic by the lime, like the carbonate itself.

Since both silicate and phosphate of potassium have an alkaline reaction and behave towards acids like the carbonate, the method of alkalimetry by neutralization is incompetent to distinguish them from the carbonate; but they do not interfere in any way with those methods of analysis which depend upon the volatilization and quantitative estimation of the Carbonic Acid in the sample. — According to Persoz (*Comptes Rendus*, 53. 239), the influence of sulphites, sulphides, and hyposulphites may be avoided, so long as the sample is free from carbon or organic matters, by using his method of fusion with bichromate of potassium (see p. 80). Fresenius destroys the sulphur compounds by igniting the weighed sample of carbonate with chlorate of potassium, before proceeding to the treatment with acid. The sulphur compounds are thus changed to inert sulphate of potassium. But if any hyposulphite be present, an equivalent quantity of the carbonate will be destroyed by its oxidation. (See Carbonate of Sodium).

For methods of determining the proportion of caustic and carbonate of potassium in a mixture of the two, like many samples of American potash, see under Alkalimetry.

In case the carbonate of potassium to be examined is contaminated with carbonate or hydrate of sodium, the proportion of potassium in the mixture may be estimated by one of the methods referred to at the close of the article Alkalimetry. According to Fresenius, the following process yields accurate results, and is tolerably expeditious:—Dissolve in water 6.25 grm. of the ignited pearlash, filter the solution into a quarter-litre flask, add acetic acid to slight excess, and warm the liquid to expel carbonic acid. After the carbonic acid has been driven off, add a solution of acetate of lead, drop by drop, to the hot liquor until the formation of a precipitate of sulphate of lead *just ceases*. Allow the mixture to cool, fill the flask with water to the mark, shake the mixture and then let it stand to settle; filter through a dry filter, and transfer 200 c. c. of the filtrate, corresponding to 5 grms. of the pearlash, to a quarter-litre flask. Fill the flask to the mark with strong sulphuretted hydrogen water and shake its contents. If the acetate of lead was carefully added the fluid will now smell of sulphuretted hydrogen and be free from lead. In case the liquid does not smell of sulphuretted hydrogen a stream of that gas must be passed through it. After the sulphide of lead has subsided, filter the liquid through a dry filter; place 50 c. c. of the filtrate, corresponding to 1 grm. of the pearlash, together with 10 c. c. of chlorhydric acid, of 1.1 sp. gr., in a weighed platinum dish, and evaporate the mixture to dryness. Cover the dish, heat the mixed chlorides moderately, and weigh them* (see Chloride of Potassium). The weight obtained expresses the amount of chloride of potassium plus chloride of sodium

given by 1 grm. of the pearlash. Determine the chlorine by titration (see Chloride of Silver) and calculate the amounts of potassium and of sodium as described under Chloride of Potassium. For a similar calculation see Carbonic Acid, indirect separation of calcium from strontium.

In case it is desired to know how much of any sample of pearlash consists of foreign salts, determine the Water contained in it, by gently heating a weighed quantity (8 or 10 grms.) in a covered platinum dish for a long time, until dew ceases to be deposited upon a piece of cold window glass held over the dish. The loss of weight will give the proportion of water. The difference between the percentage of water plus the percentage of carbonate of potassium, as above determined, and 100, will give the percentage of fixed impurity in the substance analyzed.

In the examination of ashes, or of liquors obtained by leaching ashes, it is well to weigh out or to measure 10 or 12 times as much material as has been directed under Alkalimetry, since the proportion of alkali in ashes is comparatively small.

For use as a reagent, pure carbonate of potassium may be prepared as follows:—Heat a mixture of 10 parts of purified powdered cream of tartar, 10 parts of water, and 1 part of pure strong chlorhydric acid for several hours upon a water bath, stirring the mixture frequently. Place a small filter in the throat of a capacious funnel, pour the mixture into the funnel, and let the liquid portion drain away. Level off the top of the solid matter in the funnel, and press down upon it a disk of compact filter paper turned upwards at its edges. Pour repeated small portions of cold water (iced water is best) upon the filter paper,—in order that all the chloride and phosphate of calcium and any chloride of potassium which has been formed may be removed by percolation,—until a drop of the filtrate ceases to become cloudy when acidulated with nitric acid and tested with nitrate of silver. Then dry the purified tartrate.

Prepare on the other hand, a quantity of pure Nitrate of Potassium, and dry it. Mix 2 parts of the pure tartrate of potassium with 1 part of the pure saltpetre; see to it that the mixture is completely dry; and project the mixture by small portions into a clean, bright, wrought iron pot heated to low redness. As soon as the last portion has deflagrated, heat the contents of the pot strongly until a sample of the carbonate taken from the edge of the mass yields a perfectly colorless solution with water. Then rub up the coaly mass with water, filter, wash the residue slightly and evaporate the filtrate in a porcelain, or better, a silver dish, until it is covered with a permanent crust. Stir the liquor constantly while it cools, and throw the crystalline meal into a funnel as before; allow the meal to drain, wash it some-

what, dry it by heat in a silver or porcelain dish, and preserve the powder in well stoppered bottles. The product should be white, and should give no reaction for silicic, sulphuric, chlorhydric or phosphoric acids when evaporated with chlorhydric acid, or tested with acidulated chloride of barium, nitrate of silver or molybdate of ammonium. It should give no reaction for iron when tested with sulphocyanide of potassium.

A mixture of 13 parts of carbonate of potassium and 10 parts carbonate of sodium is preferable to either of its components for decomposing silicious minerals, by way of fusion, since the mixed carbonates melt at a lower temperature than either of the carbonates taken separately. Most refractory silicates may be decomposed by fusing them with the mixed carbonates over an ordinary Berzelius lamp or simple Bunsen's burner. (See Silicates). — Instead of mixing the pure carbonates directly, the mixture may be prepared either by igniting pure Rochelle salt and lixiviating and evaporating the residue, or by deflagrating a mixture of 20 parts pure bitartrate of potassium, prepared as above, and 9 parts of pure nitrate of sodium, and proceeding as above described.

BiCarbonate of Potassium. See biCarbonate of Sodium. Compare biCarbonate of Calcium.

Carbonate of Silver.

Principle I. Power of neutralizing acids.

Application. Precise neutralization of nitric acid liquors for the purpose of precipitating phosphate of silver, as a means of separating phosphoric acid from alkalies, alkaline earths, etc.

Method. See Phosphate of Silver. — If a phosphate insoluble in water is dissolved in a slight excess of nitric acid and the solution mixed with nitrate of silver, no precipitate will fall. But, by agitating the solution for a few moments with a slight excess of carbonate of silver, it is easy to neutralize the acid and so cause the complete precipitation of the phosphoric acid (as phosphate of silver) without introducing any new or hurtful reagent. (Chancel, *Comptes Rendus*, 1859, 49. 997).

For the use of carbonate of silver for decomposing various chlorides, as one step in Græger's method of estimating combined sulphuric acid, see Chloride of Silver, insolubility of.

Principle II. Solubility in ammonia-water, and insolubility in water.

Applications. Separation of CO_2 from S_2O_2 and H_2SO_4 , in the analysis of gunpowder residues.

Method. After all the sulphur which was in the form of an alkaline sulphide has been removed as Sulphide of Cadmium, by digesting the solution with carbonate of cadmium and filtering, heat the filtrate from the sulphide of cadmium, mix it with a neutral solution of nitrate of silver and collect the

APPENDIX TO PART I.

EXAMPLES FOR PRACTICE.

Examples are here given more for the sake of roughly indicating the method which will be followed in the appendix to the finished work, than on account of any special merit which may attach to the examples themselves.

Though none of these examples can be regarded as specially difficult, the beginner, before undertaking either of them, will of course perform several simpler experiments,—such as are described in almost any treatise on quantitative analysis. See, also, a few simple examples on the next page, at the close of the list.

The following examples are taken from Part I. (pages 1 to 112). — The completed volume will contain five such parts.

Analysis of Marble.

Grind a quantity of pure white marble, or better, Iceland Spar, to powder, dry the powder at 100° and weigh out three portions of it, each of about one gramme.

Place one portion in a beaker covered with a watch glass, dissolve it in dilute chlorhydric acid and determine the calcium by precipitation, as Carbonate of Calcium.

In another portion estimate the Carbonic Acid by Johnson's method, see p. 84; and in the third portion estimate the carbonic acid by the method of absorption in alkali, see p. 91.

To control the amount of calcium, weigh out a fourth small portion (about 0.3 gm.) of the original marble, heat it intensely over a blast lamp to expel the carbonic acid, and weigh the oxide of calcium which is left. Again heat and weigh, and repeat the operations until the results of two successive weighings are the same. The amount of calcium in the residue is found by the proportion:—

$$36 \left(= \frac{\text{Molec. wt. of CaO}}{\text{CaO}} \right) : 40 \left(= \frac{\text{Wt. of an atom of Ca}}{\text{Ca}} \right) :: \frac{\text{Wt. of the residue}}{\text{the residue}} : x \left(= \frac{\text{Wt. of Ca in the residue}}{\text{the residue}} \right)$$

Valuation of Arsenious Acid.

Select a sample of arsenious acid, pure enough to volatilize completely when heated on platinum foil. Weigh out two portions of the substance, each of about 0.5 gm., and estimate the arsenic contained in them, by the methods described under Arseniate of Lead, and Arseniate of Magnesium and Ammonium.

Estimation of Lead.

Weigh out about one gramme of pure, dry nitrate of lead, dissolve it in water and determine the lead by the method described under Carbonate of Lead.

Analysis of Sulphide of Antimony.

Treat about 0.3 gm. of the pure, crystallized native sulphide, as directed under Antimony Compounds.

Estimation of Nitric Acid.

Weigh out about 0.5 gm. of pure, dry nitrate of potassium, and proceed as directed under Arsenious Acid (Method F).

Estimation of Ammonia.

Weigh out from 0.6 to 1 gm. of pure chloride of ammonium, and proceed as directed under Ammonia, volatility of (Method A).

Separation of Iron from Magnesium.

Dissolve about 0.2 gm. of the finest iron wire in chlorhydric acid mixed with nitric acid. Add to the solution about 0.8 gm. of pure, recently crystallized Epsom salt, dilute the mixture and proceed to precipitate the iron as Acetate of Iron. Determine magnesium in the filtrate as Phosphate of Magnesium and Ammonium.

Separation of Antimony from Tin.

See Antimony, Method B.

Valuation of Carbonate of Sodium.

1. By Alkalimetry, through neutralization.
2. By fusion with bichromate of potassium, see p. 80.
3. By Rumf's method, see p. 88.

Valuation of Acetic Acid.

By several of the methods described under that head.

Valuation of Bleaching Powder.

By Penot's method (the chlorine acting upon arsenious acid in an alkaline solution). See Arsenious Acid.

Valuation of Spirit.

See Alcohol, Principle III.

Separation of Magnesium from Sodium.

Weigh out from 0.3 to 0.4 grm. of pure, dry oxide of magnesium, prepared by igniting the oxalate; and about 0.5 grm. of pure, dry chloride of sodium. Dissolve the mixture in dilute chlorhydric acid, and proceed as described under Carbonate of Magnesium and of Ammonium. Determine the Sodium in the filtrate as Chloride of Sodium.

Analysis of Organic Compounds.

A. Prepare a quantity of oxalate of lead, by precipitation; wash it carefully, dry at 100° and weigh out three portions, of about 0.6 grm. each, for analysis. Burn one sample with oxide of copper, after Liebig (see Carbon, Principle II, Method 1), another by Bunsen's modification (p. 61) of that process, and a third with oxide of copper and oxygen, as explained under Method 2.

Though oxalate of lead contains no hydrogen, the student should nevertheless weigh the chloride of calcium tube before and after each combustion, in order to gain some idea of the errors which may be introduced through the absorption of atmospheric moisture by oxide of copper.

B. Weigh out about 0.4 grm. of pure, crystallized tartaric acid, which has been previously powdered and dried at 100° . Estimate

the carbon and hydrogen by Method 2, above cited. The amount of oxygen in the tartaric acid is obtained from the difference. The composition of pure tartaric acid is:—

C ₄	=	48	=	32
H ₆	=	6	=	4
O ₆	=	96	=	64
		150		100

Estimation of Carbon in Cast Iron.

See Carbon, Principle I, Methods B and C.

Separation of Bromine from Chlorine.

Dissolve about 0.8 grm. of pure bromide of potassium, and from 2 to 3 grms. of pure chloride of sodium in two or three hundred c. c. of water; precipitate with nitrate of silver (see Bromide of Silver), and treat portions of the dry, weighed precipitate as described under Bromide of Silver, Principles II and III.

Estimation of Carbonic Acid in Atmospheric Air.

By Pettenkofer's process, see page 97.

Estimation of Carbonic Acid in "Soda-water."

By the method of Fresenius, described on page 101.

Indirect separation of Barium from Strontium.

See page 80.

As examples of simpler experiments, fit for absolute beginners, may be mentioned:—

A. The precipitation of iron, by ammonia, as hydrated sesquioxide, and its estimation as ferric oxide. As the starting point, weigh out from 0.3 to 0.4 grm. of fine, tough, iron wire and dissolve it in pure, dilute chlorhydric acid mixed with a small quantity of nitric acid.

B. The estimation of sodium in chloride of sodium; by adding an excess of pure, diluted sulphuric acid to a weighed quantity (from 0.5 to 1 grm.) of pure fused chloride of sodium, evaporating to expel chlorhydric acid and the excess of sulphuric acid, and weighing the sulphate of sodium.

C. Estimation of chlorine in chloride of sodium, by precipitating, with nitrate of silver, as chloride of silver.

D. Estimation of silver in chloride of silver by decomposing the latter with pure metallic zinc, in presence of dilute sulphuric acid, and weighing the metallic silver.

FINDING LISTS,

FOR METHODS OF SEPARATING ELEMENTS.

ALUMINUM : Separation of from

As : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 , — and Arseniomolybdate of Ammonium.

Ba : See Al_2O_3 , Acetate of.

Ca : See Al_2O_3 , Acet.; — BaO , CO_2 , — and MgO , CO_2 .

Co : See Al_2O_3 , Acet.; — Na_2O , Al_2O_3 ; — BaO , CO_2 , — and CoO , CO_2 .

Fe : See Al_2O_3 , Acet.; — Na_2O , Al_2O_3 , — and BaO , CO_2 .

Li : See Al_2O_3 , Acetate of.

Mg : See Al_2O_3 , Acet.; — Na_2O , $2\text{B}_2\text{O}_3$; — BaO , CO_2 , — and MgO , CO_2 .

Mn : See Al_2O_3 , Acet.; — Na_2O , Al_2O_3 ; — BaO , CO_2 , — and MnO , CO_2 .

Ni : See Al_2O_3 , Acet.; — Na_2O , Al_2O_3 ; — BaO , CO_2 , — and NiO , CO_2 .

P : See BaO , CO_2 .

K : See Al_2O_3 , Acetate of.

Na : See Al_2O_3 , Acetate of.

Sr : See Al_2O_3 , Acetate of.

Ur : See Al_2O_3 , Acetate of.

Zn : See Al_2O_3 , Acet., — and BaO , CO_2 .

[For the decomposition of refractory aluminates see Na_2O , Al_2O_3 ; — BaO , CO_2 , — and Na_2O , $2\text{B}_2\text{O}_3$.]

AMMONIUM : Separation of from

All the elements : See Ammonia (Principle III) and Ammonium Salts.

ANTIMONY : Separation of from

Sb : See Sb_2O_3 .

As : See Na_2O , Sb_2O_5 ; — MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — Sb , — and As .

Bi : See Sb_2O_5 .

Cd : See Sb_2O_5 .

Co : See Sb_2O_5 ; — Sb_2O_3 , — and Sb .

Cu : See Sb_2O_5 ; — Sb_2O_3 , — and Sb .

Au : See Sb_2O_3 , — and Sb .

Fe : See Sb_2O_5 ; — Sb_2O_3 , — and Sb .

Pb : See Sb_2O_5 .

Mg : See Sb_2O_5 .

Mn : See Sb_2O_5 .

Hg : See Sb_2O_5 .

Ni : See Sb_2O_5 ; — Sb_2O_3 , — and Sb .

K : See Hg_2O , Sb_2O_5 .

Ag : See Sb_2O_5 ; — Sb_2O_3 , — and Sb .

Na : See Hg_2O , Sb_2O_5 .

S : See Sb_2O_3 .

Sn : See Na_2O , Sb_2O_5 , — and Sb .

Zn : See Sb_2O_5 .

ARSENIC : Separation of from

Al : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 , — and Arseniomolybdate of Ammonium.

Sb : See Na_2O , Sb_2O_5 ; — MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — Sb_2O_3 ; — Sb ; — As .

As : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 , — and As_2O_3 .

Ba : See Hg_2O , As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — K_2O , As_2O_5 ; — Ur_2O_3 , As_2O_5 ; — As ; — As_2O_3 ; — As_2O_5 ; — BaO , CO_2 , — and Arseniomolybdate of Ammonium.

Bi : See As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.

Br : See AgBr .

Cd : See Ag_2O , As_2O_5 ; — MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.

Ca: See Hg_2O , As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — K_2O , As_2O_5 ; — U_2O_3 , As_2O_5 ; — As ; — As_2O_3 ; — BaO , CO_2 , — and Arseniomolybdate of Ammonium.

Cr: See Arseniomolybdate of Ammonium.

Co: See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — Hg_2O , As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — As ; — As_2O_3 ; — BaO , CO_2 , — and Arseniomolybdate of Ammonium.

Cu: See Hg_2O , As_2O_5 ; — As_2O_5 ; — MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — K_2O , As_2O_5 ; — As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.

Fe: See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — As_2O_5 ; — K_2O , As_2O_5 ; — As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.

Pb: See Hg_2O , As_2O_5 ; — As_2O_5 ; — As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.

Mg: See Hg_2O , As_2O_5 ; — As_2O_5 ; — U_2O_3 , As_2O_5 ; — As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.

Mn: See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — K_2O , As_2O_5 ; — As ; — As_2O_3 ; — BaO , CO_2 , — and Arseniomolybdate of Ammonium.

Hg: See As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.

Ni: See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — Hg_2O , As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — As ; — As_2O_3 ; — BaO , CO_2 , — and Arseniomolybdate of Ammonium.

K: See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — Hg_2O , As_2O_5 ; — As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — U_2O_3 , As_2O_5 , — and Arseniomolybdate of Ammonium.

Ag: See As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.

Na: See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — Hg_2O , As_2O_5 ; — As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — SnO_2 , As_2O_5 ; — U_2O_3 , As_2O_5 , — and Arseniomolybdate of Ammonium.

Sr: See Hg_2O , As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — K_2O , As_2O_5 ; — U_2O_3 , As_2O_5 ; — As ; — As_2O_3 ; — BaO , CO_2 , — and Arseniomolybdate of Ammonium.

S: See As_2O_3 .

Sn: See SnO_2 , As_2O_5 , — and As .

Ur: See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 .

Zn: See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — Hg_2O , As_2O_5 ; — As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — K_2O , As_2O_5 ; — U_2O_3 , As_2O_5 ; — As ; — As_2O_3 ;

— BaO , CO_2 , — and Arseniomolybdate of Ammonium.

BARIUM: Separation of from

Al: See Al_2O_3 , Acetate of.

As: See Hg_2O , As_2O_5 ; — As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — K_2O , As_2O_5 ; — U_2O_3 , As_2O_5 ; — As ; — As_2O_3 ; — BaO , CO_2 , — and Arseniomolybdate of Ammonium.

Ca: See CO_2 , — and CaO , CO_2 .

C: See C , pp. 69, 79, 80; — and BaO , CO_2 .

Co: See BaO , CO_2 , — and CoO , CO_2 .

H: See B_2O_3 .

Fe: See Fe_2O_3 , Acet., — and BaO , CO_2 .

Mg: See BaO , CO_2 .

Mn: See BaO , CO_2 , — and MnO , CO_2 .

Ni: See BaO , CO_2 , — and NiO , CO_2 .

P: See BaO , CO_2 .

K: See BaO , CO_2 , — and MgO , CO_2 .

Na: See BaO , CO_2 .

Sr: See CO_2 , — and BaO , CO_2 .

Zn: See BaO , CO_2 .

BISMUTH: Separation of from

Sb: See Sb_2O_5 .

As: See As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.

Cd: See Bi_2O_3 , CO_2 , — and CdO , CO_2 .

Cl: See Bi .

Cu: See Bi_2O_3 , CO_2 , — and CuO , CO_2 .

Au: See Bi_2O_3 , CO_2 .

Pb: See Bi .

Mn: See Bi_2O_3 , CO_2 , — and MnO , CO_2 .

Hg: See Bi_2O_3 , CO_2 .

Ag: See Bi_2O_3 , CO_2 .

S: See Bi .

BORON: Separation of from

Most metals other than alkali-metals: See Na_2O , $2\text{B}_2\text{O}_3$, — and CO_2 .

Br: See AgBr .

K: See MgO , B_2O_3 .

Na: See MgO , B_2O_3 .

BROMINE: Separation of from

Most metals: See AgBr .

As: See AgBr .

B: See AgBr .

C: See HgBr ; — AgBr ; — Br , — and C , pp. 64, 68, 71, 73, 74.

Cl: See AgBr ; — KBr ; — NaBr , — and Br .

Cr: See AgBr .

Fl : See AgBr.
I : See KBr, — and Br.
P : See AgBr.
Si : See AgBr.
S : See AgBr.

CADMIUM : Separation of from

Sb : See Sb₂O₅.
As : See Hg₂O, As₂O₅; — MgO, (NH₄)₂O, As₂O₅; — As; — As₂O₃, — and Arseniomolybdate of Ammonium.
Bi : See Bi₂O₃, CO₂, — and CdO, CO₂.
C : See CO₂.
Cu : See CdO, CO₂, — and CuO, CO₂.
Pb : See CdO, CO₂, — and PbO, CO₂.
Mn : See CdO, CO₂, — and MnO, CO₂.

CALCIUM : Separation of from

Al : See Al₂O₃, Acet.; — BaO, CO₂, — and MgO, CO₂.
As : See Hg₂O, As₂O₅; — Fe₂O₃, As₂O₅; — K₂O, As₂O₅; — Ur₂O₃, As₂O₅; — As; As₂O₃; — BaO, CO₂, — and Arseniomolybdate of Ammonium.
Ba : See CO₂, — and CaO, CO₂.
C : — See C, pp. 69, 79, 80; — CO₂, — and CaO, CO₂.
Co : See CaO, CO₂, — and CoO, CO₂.
Fe : See Fe₂O₃, Acet., — and BaO, CO₂.
Mg : See CaO, CO₂.
Mn : See CaO, CO₂, — and MnO, CO₂.
Ni : See CaO, CO₂, — and NiO, CO₂.
P : See BaO, CO₂.
K : See BaO, CO₂; — CaO, CO₂, — and MgO, CO₂.
Na : See CaO, CO₂.
Sr : See CO₂, — and CaO, CO₂.
Zn : See CaO, CO₂.

CARBON : Separation of from

All bases : See CO₂, — and C, p. 64.
Ba : See BaO, CO₂, — and C, pp. 69, 79, 80.
B : See CO₂.
Br : See HgBr; — AgBr; — Br, — and C, pp. 64, 68, 71, 73, 74.
Cd : See CO₂.
Ca : See CO₂; — CaO, CO₂, — and C, pp. 69, 79, 80.
Cl : See C, pp. 64, 68, 71, 73, 74.
Cu : See CO₂.
H : See C.
I : See C, pp. 64, 68, 71, 73, 74.

Fe : See C, pp. 57, 58, 71, 75, 76.

Pb : See CO₂.

Mg : See CO₂, — and MgO, CO₂.

Ni : See CO₂.

N : See C, pp. 63, 68, 71, 73.

K : See CO₂; — K₂O, CO₂, — and C, pp. 69, 79, 80.

Na : See C, pp. 69, 79, 80.

Sr : See CO₂, — and C, pp. 69, 79, 80.

S : See Ag₂O, CO₂; and C, pp. 64, 71, 73, 74.

CHLORINE : Separation of from

Bi : See Bi.

Br : See AgBr; — KBr; — NaBr, — and Br.

C : See C, pp. 64, 68, 71, 73, 74.

I : See KBr, — and Br.

[For the estimation of chlorine “(chlorimetry)” see As₂O₃.]

CHROMIUM : Separation of from

As : See Arseniomolybdate of Ammonium.
Br : See AgBr.
C : See BaO, CO₂.
Fe : See BaO, CO₂.
Mn : See BaO, CO₂.
Ni : See BaO, CO₂.
Zn : See BaO, CO₂.

[For the decomposition of refractory Chromites see BaO, CO₂, — and Na₂O, B₂O₃.]

COBALT : Separation of from

Al : See Al₂O₃, Acet.; — Na₂O, Al₂O₃; — BaO, CO₂, — and CoO, CO₂.
Sb : See Sb₂O₅; — Sb₂O₃, — and Sb.
As : See MgO, (NH₄)₂O, As₂O₅; — Hg₂O, As₂O₅; — Fe₂O₃, As₂O₅; — As; — As₂O₃; — BaO, CO₂, — and Arseniomolybdate of Ammonium.
Ba : See BaO, CO₂, — and CoO, CO₂.
Ca : See CaO, CO₂, — and CoO, CO₂.
Cr : See BaO, CO₂.
Fe : See Fe₂O₃, Acet., — and BaO, CO₂.
Ni : See (CaO, CO₂; CoO, CO₂).
Sr : See CoO, CO₂.

COPPER : Separation of from

Sb : See Sb₂O₅; — Sb₂O₃, — and Sb.
As : See Hg₂O, As₂O₅; — As₂O₅; — MgO, (NH₄)₂O, As₂O₅; — K₂O, As₂O₅; — As; — As₂O₃, — and Arseniomolybdate of Ammonium.
Bi : See Bi₂O₃, CO₂, — and CuO, CO₂.

Cd : See CdO , CO_2 , — and CuO , CO_2 .

C : See CO_2 .

Pb : See CuO , CO_2 , — and PbO , CO_2 .

Mn : See CuO , CO_2 , — and MnO , CO_2 .

FLUORINE: Separation of from

Br : See AgBr .

GOLD: Separation of from

Sb : See Sb_2O_3 , — and Sb .

Bi : See Bi_2O_3 , CO_2 .

Pb : See PbO , CO_2 .

HYDROGEN (and Water): Separation of from

Ba : See B_2O_3 .

C : See C .

K : See B_2O_3 .

Na : See B_2O_3 .

Sr : See B_2O_3 .

IODINE: Separation of from

Br : See KBr , — and Br .

C : See C , pp. 64, 68, 71, 73, 74.

Cl : See KBr , — and Br .

[For the estimation of iodine, see As_2O_3].

IRON: Separation of from

Al : See Al_2O_3 , Acet. ; — Na_2O , Al_2O_3 , — and BaO , CO_2 .

Sb : See Sb_2O_5 ; — Sb_2O_3 , — and Sb .

As : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — As_2O_3 ; — K_2O , As_2O_5 ; — As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.

Ba : See Fe_2O_3 , Acet. , — and BaO , CO_2 .

Ca : See Fe_2O_3 , Acet. , — and BaO , CO_2 .

C : See C , pp. 57, 58, 71, 75, 76.

Cr : See BaO , CO_2 .

Co : See Fe_2O_3 , Acet. , — and BaO , CO_2 .

Fe : See Fe_2O_3 , Acet. ; — BaO , CO_2 , — and MgO , CO_2 .

Li : See Fe_2O_3 , Acetate of .

Mg : See Fe_2O_3 , Acet. , — and BaO , CO_2 .

Mn : See Fe_2O_3 , Acet. ; — Fe_2O_3 , As_2O_5 ; — Fe_2O_3 , Benz. ; — BaO , CO_2 , — and MnO , CO_2 .

Ni : See Fe_2O_3 , Acet. ; — Fe_2O_3 , As_2O_5 ; — Fe_2O_3 , Benz. , — and BaO , CO_2 .

P : See BaO , CO_2 .

K : See Fe_2O_3 , Acetate of .

Si : See Na_2O , $2\text{B}_2\text{O}_3$.

Na : See Fe_2O_3 , Acetate of .

Sr : See Fe_2O_3 , Acet. , — and BaO , CO_2 .

Ur : See Fe_2O_3 , Acetate of .

Zn : See Fe_2O_3 , Acet. ; — BaO , CO_2 , — and Fe_2O_3 , Benz.

LEAD: Separation of from

Sb : See Sb_2O_5 .

As : See Hg_2O , As_2O_5 ; — As_2O_3 ; — As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.

Bi : See Bi .

Cd : See CdO , CO_2 , — and PbO , CO_2 .

C : See CO_2 .

Cu : See CuO , CO_2 , — and PbO , CO_2 .

Au : See PbO , CO_2 .

Mn : See PbO , CO_2 , — and MnO , CO_2 .

Hg : See PbO , CO_2 .

Ag : See PbO , CO_2 .

LITHIUM: Separation of from

Al : See Al_2O_3 , Acetate of .

As : See Fe_2O_3 , As_2O_5 , — and Arseniomolybdate of Ammonium.

Fe : See Fe_2O_3 , Acetate of .

Si : See CaO , CO_2 , — and BaO , CO_2 .

MAGNESIUM: Separation of from

Al : See Al_2O_3 , Acet. ; — Na_2O , $2\text{B}_2\text{O}_3$; — BaO , CO_2 , — and MgO , CO_2 .

Sb : See Sb_2O_5 .

As : See Hg_2O , As_2O_5 ; — As_2O_3 ; — Ur_2O_3 , As_2O_5 ; — As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.

Ba : See BaO , CO_2 .

Ca : See CaO , CO_2 .

C : See CO_2 , — and MgO , CO_2 .

Fe : See Fe_2O_3 , Acet. , — and BaO , CO_2 .

Mn : See MgO , CO_2 , — and MnO , CO_2 .

K : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — BaO , CO_2 ; — MgO , CO_2 , — and $[\text{MgO}$, CO_2 ; $(\text{NH}_4)_2\text{O}$, CO_2].

Na : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 , — and $[\text{MgO}$, CO_2 ; $(\text{NH}_4)_2\text{O}$, CO_2].

MANGANESE: Separation of from

Al : See Al_2O_3 , Acet. ; — Na_2O , Al_2O_3 ; — BaO , CO_2 , — and MnO , CO_2 .

Sb : See Sb_2O_5 .

As : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — As_2O_3 ; — Fe_2O_3 , As_2O_5 ; — K_2O , As_2O_5 ; — As ; — As_2O_3 ; — BaO , CO_2 , — and Arseniomolybdate of Ammonium.

Ba : See BaO , CO_2 , — and MnO , CO_2 .

Bi : See Bi_2O_3 , CO_2 , — and MnO , CO_2 .

Cd : See CdO , CO_2 , — and MnO , CO_2 .
Ca : See CaO , CO_2 , — and MnO , CO_2 .
Cr : See BaO , CO_2 .
Cu : See CuO , CO_2 , — and MnO , CO_2 .
Fe : See Fe_2O_3 , Acet. ; — Fe_2O_3 , As_2O_5 ; — Fe_2O_3 , Benz. ; — BaO , CO_2 , — and MnO , CO_2 .
Pb : See PbO , CO_2 , — and MnO , CO_2 .
Mg : See MgO , CO_2 , — and MnO , CO_2 .
P : See MnO , CO_2 .
Sr : See MnO , CO_2 .
Zn : See MnO , CO_2 .

MERCURY : Separation of from

Sb : See Sb_2O_5 .
As : See As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.
Bi : See Bi_2O_3 , CO_2 .
Pb : See PbO , CO_2 .

NICKEL : Separation of from

Al : See Al_2O_3 , Acet. ; — Na_2O , Al_2O_3 ; — BaO , CO_2 , — and NiO , CO_2 .
Sb : See Sb_2O_5 ; — Sb_2O_3 , — and Sb .
As : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — Hg_2O , As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — As ; — As_2O_3 ; — BaO , CO_2 , — and Arseniomolybdate of Ammonium.
Ba : See BaO , CO_2 , — and NiO , CO_2 .
Ca : See CaO , CO_2 , — and NiO , CO_2 .
C : See CO_2 .
Cr : See BaO , CO_2 .
Co : See $[\text{CaO}$, CO_2 ; CoO , $\text{CO}_2]$.
Fe : See Fe_2O_3 , Acet. ; — Fe_2O_3 , As_2O_5 ; — Fe_2O_3 , Benz., — and BaO , CO_2 .
Sr : See NiO , CO_2 .

NITROGEN : Separation of from

C : See C , pp. 63, 68, 71, 73.
 *[For a method of estimating nitric acid, see As_2O_3].

PHOSPHORUS (and Phosphoric Acid) : Separation of from

Al : See BaO , CO_2 .
Ba : See BaO , CO_2 , — and Ag_2O , CO_2 .
Br : See AgBr .
Ca : See BaO , CO_2 , — and Ag_2O , CO_2 .
Fe : See BaO , CO_2 .
Mn : See MnO , CO_2 .
K : See Ag_2O , CO_2 .
Na : See Ag_2O , CO_2 .
Sr : See BaO , CO_2 , — and Ag_2O , CO_2 .

POTASSIUM : Separation of from

Al : See Al_2O_3 , Acetate of.
Sb : See Hg_2O , Sb_2O_5 .
As : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — Hg_2O , As_2O_5 ; — As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — U_2O_3 , As_2O_5 , — and Arseniomolybdate of Ammonium.
Ba : See BaO , CO_2 , — and MgO , CO_2 .
B : See MgO , B_2O_3 .
Ca : See BaO , CO_2 ; — CaO , CO_2 , — and MgO , CO_2 .
C : See CO_2 ; — K_2O , CO_2 , — and C , pp. 69, 79, 80.
H : See B_2O_3 .
Fe : See Fe_2O_3 , Acetate of.
Mg : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — BaO , CO_2 ; — MgO , CO_2 , — and $[\text{MgO}$, CO_2 ; $(\text{NH}_4)_2\text{O}$, $\text{CO}_2]$.
Si : See CaO , CO_2 , — and BaO , CO_2 .
 [See also Alkalimetry, for the estimation of potassium, and the separation of KHO from K_2O , CO_2 .

SILICON : Separation of from

Br : See AgBr .
Fe : See Na_2O , $2\text{B}_2\text{O}_3$.
Li : See CaO , CO_2 , — and BaO , CO_2 .
K : See CaO , CO_2 , — and BaO , CO_2 .
Na : See CaO , CO_2 , — and BaO , CO_2 .
 [For the decomposition of refractory silicates see B_2O_3 ; — Na_2O , B_2O_3 ; — BaO , CO_2 ; — CaO , CO_2 , — and K_2O , CO_2].

SILVER : Separation of from

Sb : See Sb_2O_5 ; — Sb_2O_3 , — and Sb .
As : See As ; — As_2O_3 , — and Arseniomolybdate of Ammonium.
Bi : See Bi_2O_3 , CO_2 .
Pb : See PbO , CO_2 .

SODIUM : Separation of from

Al : See Al_2O_3 , Acetate of.
Sb : See Hg_2O , Sb_2O_5 .
As : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — Hg_2O , As_2O_5 ; — As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — SnO_2 , As_2O_5 ; — U_2O_3 , As_2O_5 , — and Arseniomolybdate of Ammonium.
Ba : See BaO , CO_2 .
B : See MgO , B_2O_3 .
Ca : See CaO , CO_2 .
C : See C , pp. 69, 79, 80.
H : See B_2O_3 .

Fe : See Fe_2O_3 , Acetate of.

Mg : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 , — and $[\text{MgO}, \text{CO}_2; (\text{NH}_4)_2\text{O}, \text{CO}_2]$.

Si : See CaO , CO_2 ,—and BaO , CO_2 .

Sn : See SnO_2 , As_2O_5 .

[See also Alkalimetry, for the estimation of sodium and the separation of NaHO from Na_2O , CO_2].

STRONTIUM : Separation of from

Al : See Al_2O_3 , Acetate of.

As : See Hg_2O , As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — K_2O , As_2O_5 ; — U_2O_3 , As_2O_5 ; — As ; — As_2O_3 ; — BaO , CO_2 , — and Arseniomolybdate of Ammonium.

Ba : See CO_2 .

Ca : See CO_2 , — and CaO , CO_2 .

C : See CO_2 , — and C , pp. 69, 79, 80.

Co : See CoO , CO_2 .

H : See B_2O_3 .

Fe : See Fe_2O_3 , Acet., — and BaO , CO_2 .

Mn : MnO , CO_2 .

Ni : See NiO , CO_2 .

P : See BaO , CO_2 .

SULPHUR : Separation of from

Sb : See Sb_2O_3 .

As : See As_2O_3 .

Bi : See Bi .

Br : See AgBr .

C : See Ag_2O , CO_2 ; and C , pp. 64, 71, 73, 74.

TIN : Separation of from

Sb : See Na_2O , Sb_2O_5 , — and Sb .

As : See SnO_2 , As_2O_5 , — and As .

Na : See SnO_2 , As_2O_5 .

URANIUM : Separation of from

Al : See Al_2O_3 , Acetate of.

As : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 .

Fe : See Al_2O_3 , Acetate of.

WATER : See Hydrogen, above.

ZINC : Separation of from

Al : See Al_2O_3 , Acet., — and BaO , CO_2 .

Sb : See Sb_2O_5 .

As : See MgO , $(\text{NH}_4)_2\text{O}$, As_2O_5 ; — Hg_2O , As_2O_5 ; — As_2O_5 ; — Fe_2O_3 , As_2O_5 ; — K_2O , As_2O_5 ; — U_2O_3 , As_2O_5 ; — As ; — As_2O_3 ; — BaO , CO_2 , — and Arseniomolybdate of Ammonium.

Ba : See BaO , CO_2 .

Ca : See CaO , CO_2 .

C : See CO_2 .

Cr : See BaO , CO_2 .

Fe : See Fe_2O_3 , Acet., — Fe_2O_3 , Benz., — and BaO , CO_2 .

Mn : See MnO , CO_2 .

